THE PREPARATION AND CHARACTERIZATION OF SOME ALKOXO-NIOBIUM (IV) COMPLEXES

Thesis for the Degree of Ph. D.
MICHIGAN STATE UNIVERSITY
Rupert A. D. Wentworth
1963

ABSTRACT

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by Rupert A. D. Wentworth

A new class of crystalline niobium(IV) compounds, the pentachloroalkoxoniobates, have been prepared and characterized. The alkoxo group was either methoxo, ethoxo, or isopropoxo, while the cation was usually a large protonated organic base (alkylammonium, pyridinium, quinolinium, etc.). The color of the resulting compound is dependent on the nature of the cation.

The compounds were prepared by the electrolytic reduction of $NbCl_5$ dissolved in anhydrous alcohol saturated with anhydrous HCl, followed by the addition of a hot alcoholic HCl solution of the organic base.

Magnetic studies indicate Curie-Weiss paramagnetism and verify the presence of the niobium(IV) ion with 4 d^1 configuration. The infrared spectra of the compounds is in agreement with the formulation $[Nb(OR)Cl_5]^{-2}$, showing intense absorption in the region of 1000-1100 $cm.^{-1}$, which

is typical of the C-O stretching vibration in alkoxides, but not showing absorptions characteristic of the OH group. The C-O stretching frequency is dependent upon the nature of the cation to a small degree, while the ring C-H stretching frequency for the quinolinium compounds is shifted toward lower frequencies than that observed in $(C_9H_8N)Cl$ and $(C_9H_8N)_2CoCl_4$.

The dependence of the color upon the nature of the cation is obvious from the visible reflectance spectra of the compounds. The alkylammonium compounds show a single band at about 19,600 $cm.^{-1}$. The maxima in the spectra of the pyridinium compounds are always shifted toward higher frequencies, and are very asymmetric. The spectra of the quinolinium compounds are much more complex with a broad absorption band extending from 15,400 to about 22,100 $cm.^{-1}$. This band seemingly consists of two or three poorly resolved components.

The limited range of the available spectrophotometer (14,300 to 25,000 $cm.^{-1}$) makes unequivocal interpretation of the spectra of even the simply alkylammonium compounds impossible. However, the color dependence appears to arise from an interaction of the aromatic cations with the complex, possibly through the alkoxo oxygen, resulting in the observed

shift in the ring C-H and alkoxo C-O stretching frequencies.

Attempts to prepare the $[Nb(OR)Br_5]^{-2}$ and $[NbOCl_5]^{-3}$ anions were unsuccessful.

Further investigation of the ethyl alcohol-niobium(IV) system resulted in the isolation of $[NbCl(OC_2H_5)_3(C_5H_5N)]_2$. Forty-three isomers of this dimer are possible. The inertness of the chloride ions toward solvolysis and precipitation suggests that chloride bridging exists, reducing the number of possible isomers to five.

The complexity of the infrared spectrum in the region between 1000 and 1100 $cm.^{-1}$ is explained in terms of a non-equivalence of bonding between the oxygens and the metal ion, resulting from differing trans groups.

The diamagnetism of the dimer is thought to be a result of a direct overlap of the adjacent metal d_{xy} orbitals.

The reaction of $[NbCl(OC_2H_5)_3(C_5H_5N)]_2$ with sodium ethoxide results in the formation of $Nb(OC_2H_5)_4$, which is extremely unstable to hydrolysis and is difficult to purify. The diamagnetism of an impure sample suggests that it is also polymeric, but molecular weight studies were not attempted because of the compound's instability.

Both $[NbCl(OC_2H_5)_3(C_5H_5N)]_2$ and $Nb(OC_2H_5)_4$ are readily converted to $(C_5H_6N)_2[Nb(OC_2H_5)Cl_5]$, which demonstrates the equivalence of the oxidation state in the three compounds.

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A THESIS

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

DOCTOR OF PHILOSOPHY

Department of Chemistry

1963

ACKNOWLEDGMENT

The author wishes to express his sincere gratitude to Professor Carl H. Brubaker, Jr. for his guidance, kindness, and ready wit; and to the author's wife, Virginia, whose struggles and spartan existence made this investigation possible.

Appreciation is also extended to R. A. Wentworth and C. E. Rance for their regular monthly endowments; and to the Dow Chemical Company, the Eastman Kodak Company, and the National Science Foundation for financial assistance during the years of 1961-1963.

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INTRODUCTION

Niobium, the congener of vanadium, is commonly found in the pentavalent oxidation state. However, it has been known for some years that compounds with lower oxidation states could be prepared in either solid or aqueous phases. As early as 1878, Roscoe[1] reported the preparation of niobium trichloride by the thermal decomposition of the pentachloride, and in 1912 Ott[2] demonstrated that niobium(III) could be prepared by the electrolytic reduction of mineral acid solutions of niobium(V). Later work has confirmed the existence of the tetravalent, trivalent, divalent, and possibly the zero-valent states, and several examples of compounds containing mixed oxidation states.

Examples of compounds containing niobium(IV) have only recently been prepared and examined. Brubaker[3] prepared the first example, $NbCl_4$, by the reduction of the pentachloride with niobium metal. He described this compound as a crystalline, black material which hydrolyzes and oxidizes readily. Above 250° it disproportionates and forms the trichloride and the pentachloride. Its spectrum in

ethylene glycol monomethyl ether, which undoubtedly complexes the niobium ion in some manner, consists of a single, broad, asymmetric maximum at about 20,200 $cm.^{-1}$ (490 mμ) with a shoulder at about 16,000 $cm.^{-1}$ (625 mμ).

Later work led to the preparation of $NbBr_4$[4] and NbI_4.[5] All of the halides were found to be diamagnetic. Dahl[6] has examined the structure of NbI_4 and found it to consist of infinite linear chains of NbI_6 octahedra sharing opposite edges. The niobium atoms are shifted from the centers of the octahedra toward one another in pairs, resulting in a niobium-niobium distance of only 3.31Å. Weak metal-metal interactions which couple the unpaired electrons explain these shifts and account for the observed diamagnetism. The oxidation state of four is confirmed from the observed identical environments of the niobium atoms.

A qualitative interpretation of the nature of the bonding about each niobium atom has been given[7] in terms of simple molecular orbital theory based on octahedral symmetry. The $4d_{z^2}$ and $4d_{x^2-y^2}$ metal orbitals plus one 5s and three 5p metal orbitals interact with the orbitals of corresponding symmetry on the iodide ions to give bonding σ-type molecular orbitals. The unshared electron on each niobium can be placed in the d_{xy} orbital which overlaps with

an identical orbital on the adjacent niobium atom, giving rise to the observed diamagnetism. The unoccupied d_{xz} and d_{yz} orbitals are no doubt utilized in π-bonding with the filled π-type symmetry orbitals of the iodides.

The existence of the simple hexachloro-complexes of niobium(IV) has been noted in a phase study of the tetrachloride with alkali metal chlorides.[8] Unfortunately, the properties of these compounds were not noted.

There is also other evidence for the existence of this oxidation state. Niobium pentachloride is readily reduced by pyridine and lithium salts of dialkylamides to give $(C_5H_5N)_2NbCl_4$[9] and $Nb(NR_2)_4$,[10] respectively. The insolubility of the former has precluded a molecular weight determination, but the latter compound has been shown to be monomeric in benzene, and cannot be an equimolar combination of niobium(III) and niobium(V). Other examples of niobium(IV) are found in cyclopentadienyl compounds.[11,12] The blue-violet $(C_5H_5)_4Nb$, obtained from the reduction of the pentachloride with a large excess of C_5H_5Na is monomeric in benzene.

Polarography and spectrophotometry have also provided information about this oxidation state. Gozzi and Vivarelli[13] polarographically reduced hydrochloric acid

solutions of niobium(V) and observed the visible spectra of the reduced solutions. In 12 N HCl, for example, a red solution was obtained which had a single maximum at 20,900 $cm.^{-1}$ (478 mμ) while in 8 N HCl a blue solution was obtained with a single maximum at 14,300 $cm.^{-1}$ (700 mμ). In the more acidic solution they arbitrarily concluded that the $[NbCl_6]^{-2}$ ion is present while in the latter $[NbOCl_5]^{-3}$ or $[NbOCl_4]^{-2}$ are probable. Similar one-electron reductions have been observed in ethylenediaminetetraacetate, citrate, lactate, and gluconate solutions.[14]

The solid compounds discussed thus far bear little stoichiometric resemblance to those containing other metal ions with one d electron (d^1) e.g. metals from Groups IV B, V B, and VI B. In these compounds stabilization of the metal ions by halides, pseudohalides, or oxygen-containing ligands seems to be necessary. Only rarely is perfect cubic symmetry attained and most of the complexes exhibit strong tetragonality.

In Group IV B, only titanium(III) is found in simple complexes. Two hydrates exist, both having the stoichiometry $TiCl_3 \cdot 6H_2O$. Presumably the violet form is $[Ti(H_2O)_6]Cl_3$ and the green form is $[Ti(H_2O)_5Cl]Cl_2 \cdot H_2O$.[15] It also exists in several anionic halo-complexes, such as

$(NH_4)_3[TiF_6]$ and $Rb_2[TiCl_5(H_2O)]$.[16] The magnetic moment of this metal ion is generally very close to the spin-only value of 1.73 Bohr magnetons.[17]

Of the d^1 metal ions in Group V B, excluding niobium, only the complexes of vanadium(IV) are known. These are almost always tetragonal and are vanadyl (VO^{+2}) derivatives, although this is probably due to their method of preparation. Many different compounds are known and include aqua, chloro, sulfato, oxalato, and acetylacetonato derivatives. They are all exceptionally stable to oxidation. In general, the magnetic moment of the metal ion in these compounds is quite close to the spin-only value.[18] One example of supposed perfect cubic symmetry is $K_2[VF_6]$.[19] However, the magnetic moment is anomolously high.

Chromium(V), molybdenum(V), and tungsten(V) are found in a completely analogous series of compounds having the general stoichiometry $M'_2[MOX_5]$ (where M' is an alkali metal ion, M is the Group VI B metal ion, and X is chloride in the case of chromium(V) or fluoride, chloride, bromide, or thiocyanate in the cases of molybdenum(V) and tungsten(V)). The magnetic moment of chromium(V) in $Rb_2[CrOCl_5]$ is about 2.1 Bohr magnetons.[20] This high value is attributed to the presence of trivalent chromium. The moments of molybdenum(V)

in a great number of these compounds are very close to the spin-only value,[21] while tungsten(V) has not received a thorough treatment as yet.

Recently the compound $C_5H_6N[Mo(OCH_3)_2Cl_4]$ was prepared[22] during the course of a study of the alcoholysis of $MoCl_5$. Unfortunately, no spectra or magnetic susceptibilities are presented.

These metal ions have come under the close scrutiny of several theoretical chemists within the last year. In a series of papers[18,23,24] a complete molecular orbital treatment has been applied to $VO(H_2O)_5^{+2}$, $CrOCl_5^{-2}$, and $MoOCl_5^{-2}$. It was shown that simple crystal field theory could not be adequately utilized with these ions because of extensive π-bonding between the oxo ligand and the metal ion, so much so that the linkage is formulated as $M \equiv O$. This interaction results in a contraction along this axis which is, of course, observed in compounds such as $VOSO_4 \cdot 5H_2O$.[25]

The niobium(IV) compounds prepared during the course of this research, especially those containing the novel $[Nb(OR)Cl_5]^{-2}$ ion, are also tetragonal, although probably not as much as the oxo species of vanadium, chromium, and molybdenum, and should be useful to the theoretical chemist in attaining a more complete knowledge of the electronic structure of d^1 metal ions.

EXPERIMENTAL

Materials

Niobium Pentahalides.--Niobium pentachloride was obtained as a gift from the Diamond Alkali Company and was used without further purification. The manufacturers claim the purity of this compound was 99.8% with a maximum tantalum concentration of 0.02%.

Niobium pentabromide was prepared by elementary synthesis using niobium sheet purchased from Fairmount Chemical Company. This was claimed to have 99.8% purity and contained a maximum of 0.01% tantalum. The reaction was accomplished in a sealed, L-shaped tube so that the liquid bromine was at room temperature while the metal was held at 400°. The bromine was distilled from phosphorus(V) oxide in a vacuum line into tube containing a weighed amount of niobium. The tube had been previously dried by flaming and pumping at 0.01 mm. for four hours. The tube was then sealed under vacuum and the reaction was allowed to proceed. When all the metal had reacted, one end of the tube was cooled in an acetone-dry ice bath until all the bromine had

distilled into the cold end, which was then sealed from the pentabromide with a torch. The criterion for purity was the absence of any orange niobium oxybromide.

Substituted Ammonium Halides.--Tetramethylammonium chloride (Eastman White Label grade) was dried at 80° prior to use. Alcoholic solutions of dimethylammonium chloride were prepared by allowing a known amount of anhydrous dimethylamine to be absorbed in the alcohol saturated with HCl.

Pyridine, Quinoline, and Isoquinoline.--These were all Eastman White Label grade. Pyridine was dried by distillation from barium oxide and stored in a dry container. Quinoline and isoquinoline were used without further purification.

N-Methylpyridinium and N-Methylquinolinium Iodides.--N-Methylpyridinium iodide was prepared by allowing stoichiometric quantities of pyridine and methyl iodide to react. Two recrystallizations from ethyl alcohol-benzene mixtures gave yellow, acicular crystals, m.p. 116.5° (lit. 118°).[26]

N-Methylquinolinium iodide was prepared and purified similarly to yield white, acicular crystals, m.p. 145° (lit. 144.5°).[27]

Hydrogen Halides and Nitrogen.--Anhydrous hydrogen chloride and bromide, in cylinders were obtained from the Matheson Chemical Company and used without further purification.

Nitrogen was purified by passing General Dynamics, oil-pumped nitrogen over copper turnings at 500°. It was then bubbled through concentrated sulfuric acid and passed over anhydrous magnesium perchlorate.

Solvents.--Methyl alcohol was dried by reaction with magnesium and subsequent distillation. For the synthesis of the compounds containing the pentachloroalkoxoniobate(IV) anions, ethyl and isopropyl alcohols were dried by reaction with sodium and distilled. However, for the neutral alkoxo-chloro and alkoxo compounds, completely anhydrous alcohols were necessary. They were obtained by azeotropic distillation with benzene under a nitrogen atmosphere.

Anhydrous benzene was obtained by azeotropic distillation with ethyl alcohol. Chloroform was dried over calcium chloride and distilled prior to use.

Analytical Methods

Niobium and Halide Analyses.--Samples of the complexes were oxidized in very dilute nitric acid, made basic with aqueous ammonia, and digested on a steam bath for several hours.

With the compounds $[NbCl(OC_2H_5)_3(C_5H_5N)]_2$ and $Nb(OC_2H_5)_4$, which are insoluble in water, a better procedure consisted of dissolution in a small amount of ethyl alcohol, addition of about 10 ml. of 1 M ammonia, followed by evaporation to dryness on a steam bath. The residue was then treated in exactly the same manner as the water-soluble complexes.

The solutions were adjusted to pH = 1 with nitric acid and filtered to remove the hydrous niobium pentoxide. Niobium was determined gravimetrically by ignition of the hydrous oxide. Chloride or bromide was determined by potentiometric titration of the filtrate with standardized $AgNO_3$.

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

Pyridine Analysis.--In several instances, a rapid method for the determination of the pyridine content of a compound was desirable. Accordingly, the following spectrophotometric method was developed. Solutions of pyridine up to 1.7×10^{-4} M in 0.05 N H_2SO_4 were found to obey Beer's Law at 255 mμ ($\epsilon = 5.01 \times 10^3$ l. mole^{-1} cm.$^{-1}$). Samples were digested in aqueous solutions of H_2SO_4 of known concentration, filtered; and the solutions were made up to one liter with

sufficient H_2SO_4 and water so that the final concentration was 0.05 N. The pyridine content was determined spectrophotometrically at 255 mμ.

Alkoxide Determination.--The ethoxide content in $Nb(OC_2H_5)_4$ was determined by the quantitative oxidation of ethyl alcohol with $K_2Cr_2O_7$.[45] To a weighed sample of the tetraethoxide, a weighed amount of $K_2Cr_2O_7$ was added and several ml. of 12.5% H_2SO_4 was added. After two hours the unreacted Cr(VI) was determined iodometrically.

Determination of the Oxidation State of Niobium.--The oxidation state of a few samples was determined by oxidation of the compound with standard aqueous $K_2Cr_2O_7$, followed by back titration of the excess Cr(VI) with a standard solution of $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$. The end point was determined amperometrically using a rotating platinum electrode and a calomel reference electrode. The current was measured with the galvonometer of a Sargent Model XXI polarograph.

Molecular Weight.--The molecular weight of $[NbCl(OC_2H_5)_3(C_5H_5N)]_2$ was determined ebullioscopically by Huffman Microanalytical Laboratories, Wheatridge, Colorado. Due to the sensitivity of the compound to oxidation, the measurement was performed

in a dry nitrogen atmosphere. The stated precision was ± 10%.

Electrolysis Apparatus

The electrolysis vessel (Figure 1) consisted of a 125 ml. Erlenmeyer flask with a ground glass top. The flask was fitted with a two-way stopcock on the bottom, and a bent side-arm which contained a fine porosity fritted glass disc. The vertical portion of the side-arm served as the anode compartment. The level of the mercury pool cathode could be adjusted by a leveling bulb which was connected to one arm of the two-way stopcock by a short piece of flexible tubing. The anode compartment contained the appropriate alcohol saturated with HCl and a short piece of carbon rod which served as the anode. The solution was stirred during the electrolysis by bubbling dry, purified, nitrogen through the electrolyte and allowing it to escape through an opening in the top of the flask. The nitrogen also served to exclude air and moisture.

The current was provided by a Heathkit variable voltage power supply (Model PS-3) capable of producing a maximum current of 0.2 amp.

Figure 1. Electrolysis vessel.

Preparation of Compounds

Attempts to Prepare Solid Compounds Containing a Reduced Niobium Species from Aqueous Solutions. Sulfuric Acid Solution.--Sulfuric acid solutions of niobium(V) were prepared by dissolving hydrous niobium pentoxide[28] (containing between 30-40% H_2O) in concentrated H_2SO_4 at 210° with stirring, cooling to 0°, and slowly adding water dropwise to the solution. It was found after repeated attempts that an acid concentration of 6 M was necessary to prevent precipitation in solutions that were 0.04 M in niobium.

A solution of these concentrations was electrolyzed at 6.7 volts and a current density of 0.003 amp/cm.^{2}. Titration showed the niobium to be trivalent. The solution was blue and this color was retained on an anion exchange column, but was readily eluted with water. Attempts were next made to precipitate the anion using cations of varying size and charge. The addition of Na^+, K^+, NH_4^+, $(CH_3)_4N^+$, $[Co(en)_3]^{+3}$, $[Co(NH_3)_5Cl]^{+2}$, and $[Co(en)_2(C_2O_4)]^+$ in 3 M H_2SO_4 failed to produce any precipitate even when present in large excess.

Hydrochloric Acid Solutions.--Solutions that were 0.005M in niobium(V) were easily prepared by the solution of the

pentachloride in concentrated aqueous HCl. Electrolysis over extended periods of time at a potential of about 10 volts and a current of 0.15 amp. produced solutions containing trivalent niobium.

When these solutions were evaporated in a vacuum, a bright blue cake would form before the solvent was completely removed. This product was amorphous and contained only small amounts of chloride ion. It is undoubtedly a hydrous oxide formed by the hydrolysis of the anionic chloro-niobium species.

Attempts were made to precipitate this anionic species by the addition of Na^+ or K^+ ions and saturation of the solution with HCl at -20° with no success.

It is unfortunate that the limited supply of the pentachloride at that time prevented a more detailed study at higher niobium concentrations.

Compounds Containing the Pentachloroalkoxoniobate(IV) Anion.

Because of the lack of success in preparing simple complexes in aqueous solutions, the electrolysis of alcohol-HCl solutions of niobium(V) was investigated as a possible route to such complexes.

Methoxo complexes. Pyridinium Pentachloromethoxoniobate(IV).-- A complete description of the preparation of this compound

will be given and applies to the preparation of all the complexes of this type. A solution of niobium(IV) was prepared by the electrolytic reduction of the pentachloride (4.0 g., 0.015 mole) in 25 ml. of anhydrous methyl alcohol. The potential was adjusted so that a current of 0.075 amp. was maintained throughout the electrolysis. The solution rapidly became wine-red and then changed to deep brown after several hours. No hydrogen evolution was noted until about the theoretical time for a one-electron reduction. Concurrently, the thin layer of solution between the flask and the meniscus of the mercury became yellow while the bulk of the solution remained dark brown. Titration experiments with portions of the solution showed that the niobium was completely tetravalent at this point. On one occasion, the period of electrolysis was extended by 300%, but no further reduction of the niobium was noted.

The mercury was then removed and the solution drained into a flask containing slightly more than the stoichiometric quantity of pyridine in hot methyl alcohol saturated with HCl. The compound which resulted after several hours of cooling, was obtained as a red-brown, spiny, crystalline agglomerate. Filtration was accomplished under a nitrogen atmosphere. The crystals were washed with three 20 ml. portions of chloroform,

and dried by continuous pumping for 24 hours.

Anal. Calcd. for $(C_5H_6N)_2[Nb(OCH_3)Cl_5]$:C, 28.61; H, 3.27; Cl, 38.45; Nb, 20.13, C_5H_5N, 34.3. Found: C, 28.67; H, 3.30; Cl, 38.21; Nb, 20.21, C_5H_5N, 34.7. Oxidation state: 4.03.

When larger excesses of pyridine were used in the precipitation, the product was an amorphous, brown cake. When cold methyl alcohol was substituted for chloroform in the washing of the crystals, the chloride to niobium ratio was only 4.88 indicating that some solvolysis had probably occurred.

Tetramethylammonium pentachloromethoxoniobate(IV).--Pink crystals after a few minutes. Anal. Calcd. for $[(CH_3)_4N]_2[Nb(OCH_3)Cl_5]$: Cl, 39.5; Nb, 20.68. Found: Cl, 39.1; Nb, 20.77.

Quinolinium pentachloromethoxoniobate(IV).--Violet crystals after 20 min. Anal. Calcd. for $(C_9H_8N)_2[Nb(OCH_3)Cl_5]$: Cl, 31.6; Nb, 16.55. Found: Cl, 31.2; Nb, 16.71.

Isoquinolinium pentachloromethoxoniobate(IV).--Red crystals after 10 min. Anal. Calcd. for $(C_9H_8N)_2[Nb(OCH_3)Cl_5]$: Cl, 31.6; Nb, 16.55. Found: Cl, 31.2; Nb, 16.58.

Ethoxo Complexes. Dimethylammonium pentachloroethoxoniobate(IV).--Peach needles within one minute. Anal. Calcd. for $[(CH_3)_2NH_2]_2[Nb(OC_2H_5)Cl_5]$: Cl, 43.5; Nb, 22.80. Found: Cl, 43.5; Nb, 22.87.

Pyridinium pentachloroethoxoniobate(IV).--Orange crystals within a few minutes. Anal. Calcd. for $(C_5H_6N)_2[Nb(OC_2H_5)Cl_5]$: C, 30.30; H. 3.56; Cl, 37.33; Nb, 19.54. Found: C, 30.62; H, 3.71; Cl, 37.21; Nb, 19.41.

N-Methylpyridinium pentachloroethoxoniobate(IV).--Red crystals after 5 min. Anal. Calcd. for $(C_6H_8N)_2[Nb(OC_2H_5)Cl_5]$: Cl, 35.3. Found: Cl, 35.0.

4-Picolinium pentachloroethoxoniobate(IV).--Orange crystalline polyhedra after a few minutes. Anal. Calcd. for $(C_6H_8N)_2[Nb(OC_2H_5)Cl_5]$: Cl, 35.3; Nb, 18.45. Found: Cl, 35.5; Nb, 18.59.

Quinolinium pentachloroethoxoniobate(IV).--Crystallization of this violet compound was initiated by cooling at -77° until one crystal formed, and holding the solution at -10° for several hours. Anal. Calcd. for $(C_9H_8N)_2[Nb(OC_2H_5)Cl_5]$: C, 42.91; H, 3.79; Cl, 30.80; Nb, 16.12. Found: C, 42.88;

H, 3.67; Cl, 30.44; Nb, 15.73.

N-Methylquinolinium pentachloroethoxoniobate(IV).--Violet crystals after 10 min. Anal. Calcd. for $(C_{10}H_{10}N)_2[Nb(OC_2H_5)Cl_5]$: Cl, 29.40. Found: Cl, 29.5.

Isopropoxo complexes. Tetramethylammonium pentachloroisopropoxoniobate(IV).--Pink curdy precipitate immediately. This was not investigated further.

Pyridinium pentachloroisopropoxoniobate(IV).--Orange powder formed immediately. Anal. Calcd. for $(C_5H_6N)_2[Nb(OC_3H_7)Cl_5]$: Cl, 36.3; Nb, 18.98. Found: Cl, 35.9; Nb, 19.10.

Quinolinium pentachloroisopropoxoniobate(IV).--Violet powder formed immediately. Anal. Calcd. for $(C_9H_8N)_2[Nb(OC_3H_7)Cl_5]$: Cl, 30.1; Nb, 15.76. Found: Cl, 30.0; Nb, 15.86.

Physical Properties of the Pentachloroalkoxoniobates.--They are extremely sensitive to air, turning blue and then white. They are soluble in water to give a brown solution from which slowly deposits a hydrous brown oxide. In alcohols, solution is accompanied by decomposition; and the color of the solution depends on the water content of the alcohol. If the alcohol is completely anhydrous, the solution is blue; but in the

presence of traces of water, the color is brown.

In dimethylformamide, the solution is initially violet, but quickly changes to blue. These solutions are extremely sensitive to oxidation, however, and would require the utmost care in handling.

They are insoluble in dimethylsulfoxide, and common organic solvents, such as benzene, ethers, and ketones.

Attempts to Prepare Analogous Bromo Complexes.

Several attempts to prepare compounds containing the $[Nb(OC_2H_5)Br_5]^{-2}$ ion, by the electrolytic reduction of the pentabromide in ethyl alcohol saturated with HBr, failed. Crystalline substances containing no definite bromide to niobium ratio were obtained when the pyridinium and quinolinium cations were employed. For example, the material containing the pyridinium ion had a Br/Nb ratio of 5.74. Significantly, both substances were green and their infrared spectra showed no alkoxo groups to be present.

Attempts to Prepare Compounds Containing the $[NbOCl_5]^{-3}$ Ion.

Several attempts to prepare compounds of this class failed. Two basic methods were tried and will be described.

When 95% and 90% ethyl alcohol solutions (saturated with HCl) of $NbCl_5$ (0.6 M) were electrolyzed and added to

stoichiometric quantities of pyridine in the same solvent, the product in both cases $(C_5H_6N)_2[Nb(OC_2H_5)Cl_5]$. This was verified in both cases by the infrared spectra and by analysis in former case. Anal. Calcd.: Cl, 37.3. Found: Cl, 36.9.

From an 80% ethyl alcohol solution (saturated with HCl) having the same niobium concentration, a very dark green solution was obtained after electrolysis and the addition of pyridine. A dark powder precipitated upon cooling. After washing with two portions of freshly distilled chloroform and drying by continuous pumping, a pale olive cake was obtained. Its infrared spectrum showed no alkoxide to be present, but the analytical data left considerable doubt concerning the true nature of the product. Anal. Found: Cl, 28.0; Nb, 30.1; Cl/Nb, 2.43.

When the hydrolysis of several of the alkoxo compounds was attempted with aqueous HCl (oxygen-free) in the presence of stoichiometric quantities of the organic base, considerable oxidation always occurred even when extreme precautions were taken to exclude oxygen.

Preparation and Properties of Dichlorohexaethoxobis(pyridine)-diniobium(IV).

Preparation.--Niobium pentachloride (6.20 g., 0.0229 mole)

in 25 ml. of anhydrous ethyl alcohol saturated with anhydrous HCl was reduced electrolytically, and the resulting solution evaporated to dryness. The tacky, dark substance which resulted was dissolved in 20 ml. of anhydrous ethyl alcohol and 5 ml. of pyridine was added. The color of the solution changed from a deep purple to an equally deep yellow-red. Crystallization began within one hour, and was seemingly complete after another nine hours. The red compound was collected on a filter under nitrogen atmosphere and washed with three 10 ml. portions of cold ethyl alcohol; yield, 5.04 g. (64% based on $NbCl_5$). Concentration of the mother liquor produced only a small amount of the compound.

Anal. Calcd. for $[NbCl(OC_2H_5)_3(C_5H_5N)]_2$: C_5H_5N, 23.1; Cl, 10.4; Nb, 27.1. Found: C_5H_5N, 23.2; Cl, 10.3; Nb, 27.1. Molecular weight calcd. for dimer: 686. Ebullioscopic molecular weight in $CHCl_3$: 674. Molecular complexity: 1.97.

The dimer is very soluble in chloroform, and slightly soluble in ethyl and isopropyl alcohols at room temperature. It is insoluble in acetone, benzene, carbon tetrachloride, nitrobenzene, dimethylsulfoxide, dimethylformamide, 1,4-dioxane, glacial acetic acid, methylene

chloride, 1,1',1"-trichloroethane, and pentachloroethane. In oxygen-free water, it is insoluble.

When heated in a sealed evacuated tube, this compound turns brown at about 100° and liquifies with gas evolution (pyridine ?) at about 155°.

Reaction of $[NbCl(OC_2H_5)_3(C_5H_5N)]_2$ with Pyridinium Ion in Alcoholic HCl. A Demonstration of the Oxidation State of Niobium in the Dimer.--To 5 ml. of ethyl alcohol saturated with HCl, 0.20 g. of the dimer was added. The mixture was heated gently to accelerate the solution process, and the color of the solution changed from purple to ochre. Pyridine (0.2 ml.) was added, and the solution cooled at -10° for twenty-four hours. The small, bright orange crystals were collected on a filter under nitrogen, washed with two 10 ml. portions of $CHCl_3$, and dried by continuous pumping for twelve hours; yield, 0.12 g. (43% based on the dimer). The infrared spectrum of this compound was identical to that of an authentic sample of $(C_5H_6N)_2[Nb(OC_2H_5)Cl_5]$. Anal. Calcd. for $(C_5H_6N)_2[Nb(OC_2H_5)Cl_5]$: Cl, 37.3. Found: Cl, 36.8.

Attempted Solvolysis of $[NbCl(OC_2H_5)_3(C_5H_5N)]_2$ with Isopropyl Alcohol.--A small amount of the dimer (ca. 0.1 g.) was heated

to 150° in a sealed, evacuated tube with 25 ml. of isopropyl alcohol for twenty-four hours. The tube was then opened in a nitrogen atmosphere, the solvent was distilled away and a brown, tacky substance remained. Large amounts of pyridine were found in the distillate. Analysis of the residue indicated that no solvolytic replacement of chloride had occurred, and that the nature of the residue was uncertain. Anal. Calcd. for $NbCl(OC_2H_5)_3(C_3H_7OH)$: Cl, 11.0; Nb, 29.5. Calcd. for $NbCl(OC_3H_7)_3$: Cl, 11.5; Nb, 30.1. Found: Cl, 11.7; Nb, 28.7; Cl/Nb, 1.07.

Attempts to Precipitate Chloride Ion from $[NbCl(OC_2H_5)_3(C_5H_5N)]_2$ with Alcoholic Solutions of $AgNO_3$ and KI.--When a concentrated alcoholic solution of $AgNO_3$ was added to a small amount of the dimer dissolved in anhydrous ethyl alcohol, immediate decolorization of the solution occurred and was accompanied by the precipitation of a gray material along with a milky solid. The gray solid was separated by filtration and washed successively with alcohol and aqueous ammonia. Qualitative analysis indicated it to be silver metal.

A saturated solution of KI was added to a solution of the dimer without producing any visible effect, even after heating for several minutes. If a labile chloride

ion had been present, then a precipitate of KCl would have been expected.

Preparation and Reactions of Tetraethoxoniobium(IV).

Preparation. Attempts by the Ammonia Method.--When an electrolytically reduced solution of $NbCl_5$ (2.7 g., 0.0010 mole) in 25 ml. of anhydrous ethyl alcohol saturated with HCl was evaporated to dryness, a tacky, dark, unknown substance was obtained in which the Cl/Nb ratio approximated two. The passage of large quantities of gaseous ammonia, which was distilled from sodium, into a solution of the substance in 20 ml. of ethyl alcohol and 20 ml. of benzene resulted in the precipitation of NH_4Cl, but without any noticeable change in the color of the solution. The solution was filtered, and evaporated to give a brown solid containing 8.63% Cl.

Preparation by the Reaction of $[NbCl(OC_2H_5)_3(C_5H_5N)]_2$ with $NaOC_2H_5$.--In a typical preparation, 4.97 g. (0.00724 mole) of $[NbCl(OC_2H_5)_3(C_5H_5N)]_2$ was added to a hot solution of 0.01448 mole of $NaOC_2H_5$ in 50 ml. of anhydrous ethyl alcohol. The bright blue precipitate, which formed initially, slowly disappeared and a deep red-brown solution formed. This was evaporated to dryness and the residue dissolved in 40 ml. of benzene. This solution was filtered to remove NaCl, and

evaporated under vacuum at 60° to yield an extremely hydroscopic red-brown oil.

Anal. Calcd. for $Nb(OC_2H_5)_4$: Nb, 34.1; Cl, 0.00. Found: Nb 35.9; Cl, 0.34. In a second preparation, found: Nb, 33.0; Cl, 0.47.

Exposing the substance for short periods of time to the so-called anhydrous nitrogen atmosphere of a dry box caused the color to change to deep brown and the niobium content to rise steadily, indicating that hydrolysis was occurring.

A quantity of the oil was placed in a sublimator which contained a dry ice-ethylene glycol monomethyl ether (methyl cellosolve) coolant in the cold-finger. A tacky, red-brown solid began to collect on the cold finger at 0.002 mm. and a bath temperature of 160°. A dark brown solid residue remained in the sublimator.

Anal. Calcd. for $Nb(OC_2H_5)_4$: Nb, 34.1, OC_2H_5 , 65.9 Cl, 0.00. Found: Nb, 34.5; OC_2H_5, 64.9; Cl, 0.00; OC_2H_5/Nb, 3.90.

Reaction of $Nb(OC_2H_5)_4$ with Pyridinium Ion in Alcoholic HCl. A Proof of the Oxidation State of Niobium.--Unsublimed $Nb(OC_2H_5)_4$ (0.15 g., 0.00055 mole) was dissolved in 3 ml.

of anhydrous ethyl alcohol saturated with HCl, and 0.2 ml. of pyridine were added. The color of the solution changed from deep brown to ochre. The solution was cooled at -10° for forty-eight hours. The small, orange crystals were collected on a filter under nitrogen, washed with two 10 ml. portions of $CHCl_3$, and dried in a vacuum overnight. The infrared spectrum was identical to that of an authentic sample of $(C_5H_6N)_2[Nb(OC_2H_5)Cl_5]$. Total yield: 0.23 g. (89% based on $Nb(OC_2H_5)_4$). Anal. Calcd. for $(C_5H_6N)_2[Nb(OC_2H_5)Cl_5]$: Cl, 37.3. Found: Cl, 37.2.

Spectroscopic Measurements

The complete infrared spectra of the compounds were obtained in Nujol mulls and the use of a Perkin-Elmer Model 21 spectrophotometer. The spectra from 2400-3600 $cm.^{-1}$ were obtained with perfluorokerosene mulls and a Beckman IR-7 spectrophotometer. The mulls were prepared in a dry box under a nitrogen atmosphere.

The visible solution spectra were obtained with a Beckman Model DK-2 spectrophotometer, while the reflectance spectra were obtained with a Bausch and Lomb spectrophotometer with a reflectance attachment. $MgCO_3$ was used as a standard. In order to prevent oxidation of the solid

samples, they were ground with mineral oil and spread between two circular, microscope cover glasses.

Magnetic Moment Measurements

Magnetic susceptibilities were measured by the Gouy method using the apparatus and techniques of Vander Vennen.[29] The calculation was facilitated by use of the equation:[30]

$$10^6 X = \frac{\alpha + \gamma F'}{w} \qquad (1)$$

where X is the gram-susceptibility of the sample; α is a constant related to the volume of displaced air, and is simply 0.029 x sample volume; γ is the tube constant; F' is the force experienced by the sample alone, i.e., the measured force corrected for the force experienced by the tube alone; and w is the sample weight.

In practice the constant γ must be determined for a particular tube using a material of known susceptibility. In this research freshly distilled water was used, whose susceptibility is known to be -0.720×10^6 with $dX/dt = 0.0012$/degree at 20^o.[31]

The molar susceptibility of the sample is obtained by multiplying the gram-susceptibility by the molecular weight. The susceptibility of the metal ion X'_M is

obtained simply by correction of the molar susceptibility for any diamagnetic species present. Pascal's constants[32] were used in this research to estimate the diamagnetism of the ligands and cations, with the exception of the pyridinium and quinolinium ions. The values for these were obtained from Holm and Cotton.[33]

In normal paramagnetic substances X'_M is related simply to the absolute temperature as

$$X'_M = \frac{C}{T} \quad \text{(Curie Law)} \tag{2}$$

or

$$X'_M = \frac{C}{T + \theta} \quad \text{(Curie-Weiss Law)} \tag{3}$$

For the latter case a plot of $1/X'_M$ against T allows the evaluation of C and θ from the slope and intercept.

A quantity which is most familiar to chemists is the magnetic moment μ of an ion, which is related to X'_M as

$$X'_M = \frac{N\mu^2\beta}{3kT} \quad \text{or} \quad \frac{N\mu^2\beta}{3k(T+\theta)} \tag{4}$$

It is easily seen by comparing (2) or (3) with (4) that

$$C = \frac{N\mu\beta}{3k} \tag{5}$$

where N is Avagadro's number; β is the Bohr magneton; and k is Boltzmann's constant. Simplification leads to

$$\mu = 2.84\, C^{1/2} \tag{6}$$

Since the alkoxo compounds are extremely sensitive to oxidation and hydrolysis, it was necessary that they be protected from the atmosphere during a measurement. After γ was experimentally determined, the tube was carefully filled with the ground sample and then sealed. A knowledge of the weights of the filled tube and glass fragment allowed the calculation of the sample weight.

The low-temperature studies were performed using a specially constructed Dewar flask[29] and methyl cellosolve-dry ice and liquid nitrogen coolants.

The results are shown in Table I. The susceptibilities of the pentachloroalkoxoniobates follow the Curie-Weiss Law in all cases, and correspond closely to the spin-only moment for a d^1 metal ion.

One preparation of $[NbCl(OC_2H_5)_3(C_5H_5N)]_2$ was slightly paramagnetic, while another was strongly diamagnetic. The positive value can undoubtedly be attributed to paramagnetic impurities. Since the magnetic purity of even the second sample was unknown, it must be regarded as only an indication of the diamagnetism of the dimer. Similarly, due to the small supply of relatively pure $Nb(OC_2H_5)_4$ and its extreme instability to hydrolysis, the sample was impure and the susceptibility can only be taken as an indication of complete spin-pairing.

Table I. Magnetic susceptibilities and moments of some of the alkoxo-niobium(IV) compounds.

Compound	Temp. °A	Susceptibility $X'_M \times 10^6$	θ °A	μ
$(C_5H_6N)_2[Nb(OCH_3)Cl_5]$	299	1020	61	1.72
	196	1430		
	77	2700		
$(C_9H_8N)_2[Nb(OC_2H_5)Cl_5]$	298	1150	19	1.72
	196	1690		
	77	3660		
$(C_9H_8N)_2[Nb(OC_3H_7)Cl_5]$	296	1210	20	1.74
	196	1790		
	77	3620		
$[NbCl(OC_2H_5)_3(C_5H_5N)]_2$	296	13		
	299	-1150		
$Nb(OC_2H_5)_4$	299	-100(in C_6H_6)		

The magnetic moments are estimated to have a precision of ± 3%, based on a duplicate determination of $(C_5H_6N)_2[Nb(OCH_3)Cl_5]$.

Attempts to Obtain X-Ray Diffraction Data

Numerous attempts were made to obtain X-ray powder photographs of $(C_5H_6N)_2[Nb(OCH_3)Cl_5]$ and $[NbCl(OC_2H_5)_3(C_5H_5N]_2$ using the ground powders in sealed 0.3 mm. glass capillary tubes, and a Debye-Scherrer camera with Cr K_α radiation. In both cases, the samples were completely white after the necessary long exposure time. The films did contain some lines which were almost unreadable. It is not known whether the decomposition is a result of the X-ray irradiation or slow oxidation by the diffusion of oxygen through the thin, glass capillary.

DISCUSSION OF RESULTS

The Pentachloroalkoxoniobates

During the course of this research, twelve crystalline niobium(IV) compounds, all having the general stoichiometry of $(BH)_2[Nb(OR)Cl_5]$, were prepared and characterized. One previous example of this class, $(C_5H_6N)_2[Zr(OC_2H_5)Cl_5]$, is known.[34] The cationic portion of the niobium compounds always consisted of a large organic cation (alkylammonium, pyridinium, quinolinium, etc.), while the alkoxo group was either methoxo, ethoxo, or isopropoxo. The color of the resulting compound is dependent on the nature of the cation.

Conclusive evidence that the compounds contain pyridinium and quinolinium ions and not ligand pyridine and quinoline is readily had by comparing the infrared spectra of the compounds with those of $(C_5H_6N)Cl$, $(C_5H_6N)_2CoCl_2$,[35] $(C_9H_8N)Cl$, $(C_9H_8N)_2CoCl_4$,[36] and $(C_9H_7N)_2CoCl_2$[37] (Tables 2 and 3). Further support is to be had from the analogous N-methylpyridinium and N-methylquinolinium compounds, which cannot be coordinated to the metal ion through nitrogen.

Table 2. A comparison of the infrared spectra of pyridinium ion and ligand pyridine with that of $(C_5H_6N)_2[Nb(OCH_3)Cl_5]$.

$C_5H_6N^{+35}$	ligand C_5H_5N	$(C_5H_6N)_2[Nb(OCH_3)Cl_5]$
1630 s	1600 s	1630 s
1600 s	1570 w	1600 s
1530 s	1490 s	1525 s
1480 s	1440 s	1475 s
1325	----	1335 m
1240 m	1240 vw	1240 m
1200 m	1215 s	1195 m
1160 m	1150 m	1160 m

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

Table 3. A comparison of the infrared spectra of quinolinium ion and ligand quinoline with that of $(C_9H_8N)_2[Nb(OCH_3)Cl_5]$.

$C_9H_8N^+$	ligand C_9H_7N	$(C_9H_8N)_2[Nb(OCH_3)Cl_5]$
1630 s	1590 s	1630 s
1590 s	1580 m	1590 s
1550 s	1540 s	1550 s
1400 s	1400 m	1410 s
1300 s	1320 s	1300 s
1220 s	1310 s	1230 s
1160 m	1140 m	1160 w
1140 m	1130 m	1140 m
1080 m	1080 m	1070 m

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

However, the infrared spectra (Figure 2) of the quinolinium compounds does show some irregularities in the ring C-H stretching frequency. In both $(C_9H_8N)Cl$ and $(C_9H_8N)_2CoCl_4$ this vibration occurs at 3400 $cm.^{-1}$ (Figure 3), and is seemingly sharp and without fine structure. In the niobium compounds this absorption has shifted to 3000 $cm.^{-1}$ and exhibits considerable fine structure. This indicates a weakening of the ring C-H bond. The possible cause will be outlined after a consideration of other aspects of the spectra of these compounds.

Alcohols uniformly have intense absorptions in the region of 1100 $cm.^{-1}$ which have been assigned to the C-O stretching vibration. Such an absorption is present in all the pentachloroalkoxoniobates; and since there is no indication of the O-H vibrational mode, the alkoxide ion must be directly coordinated to the metal ion. The absorptions associated with the C-O stretching vibration are not constant for a given alkoxide, but seem to depend, at least to a small extent, on the nature of the cation. Exact frequencies from the spectra presented in Figure 4 through 10 are: $[(CH_3)_4N]_2[Nb(OCH_3)Cl_5]$, 1130 $cm.^{-1}$; $(C_5H_6N)_2[Nb(OCH_3)Cl_5]$, 1095 $cm.^{-1}$;

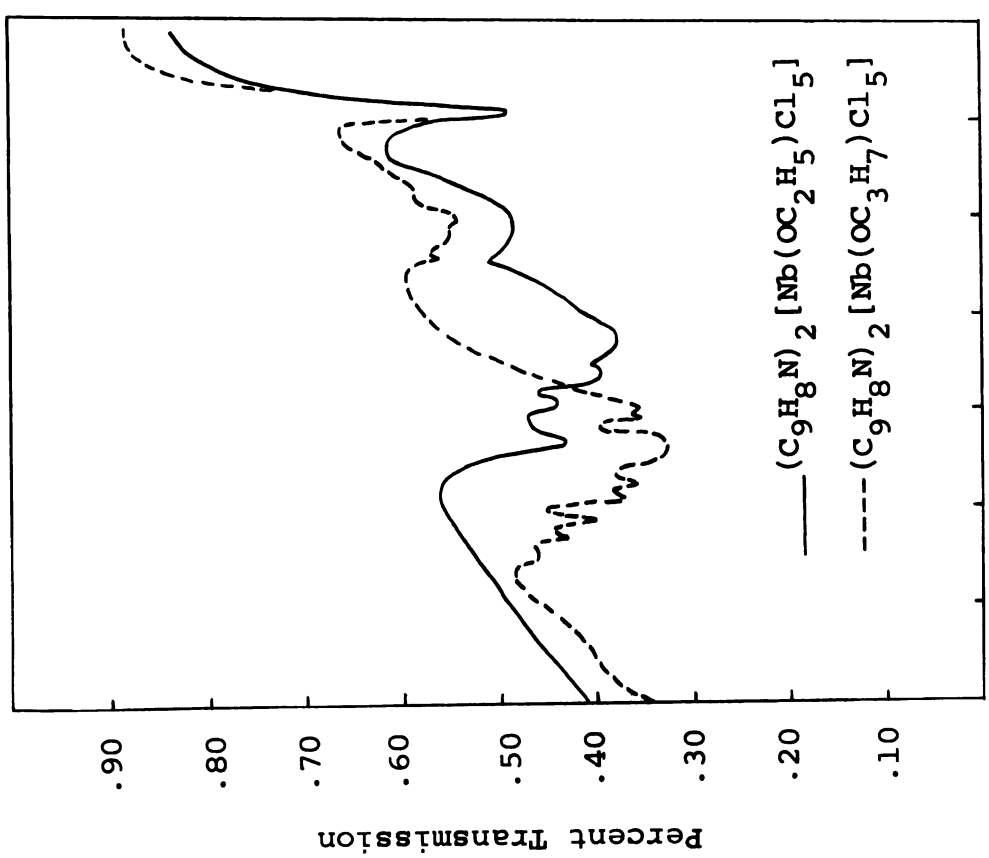


Figure 2. Infrared spectra of $(C_9H_8N)_2[Nb(OC_2H_5)Cl_5]$ and $(C_9H_8N)_2[Nb(OC_3H_7)Cl_5]$ from 2200 to 3600 $cm.^{-1}$ (Perfluorokerosene mull).

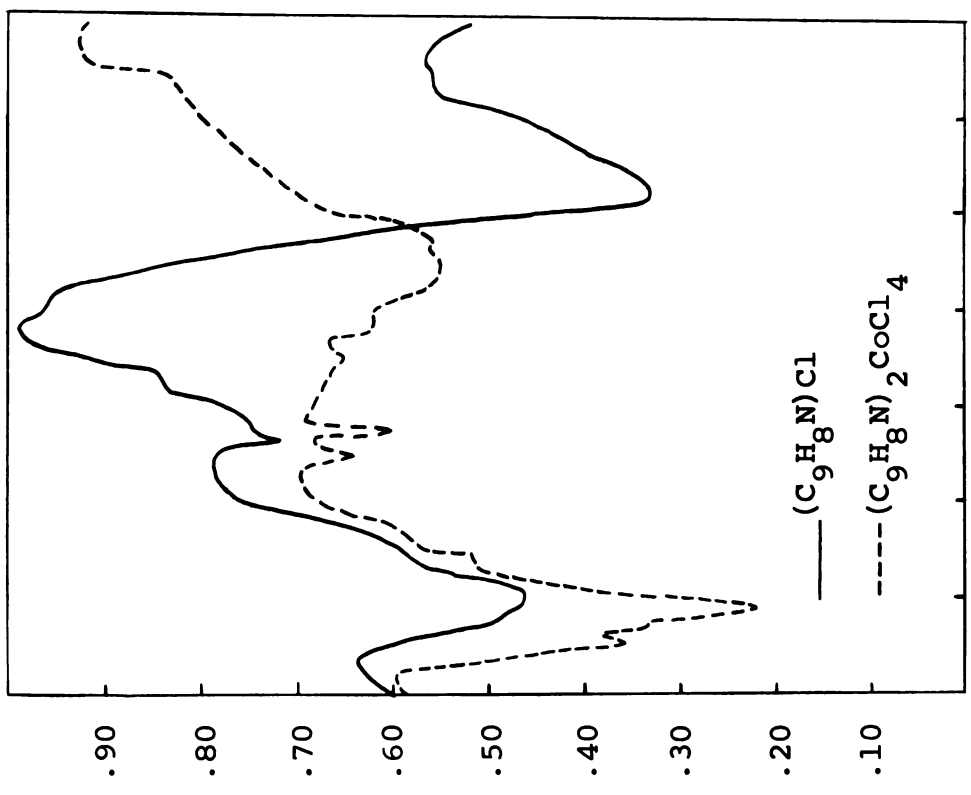


Figure 3. Infrared spectra of $(C_9H_8N)Cl$ and $(C_9H_8N)_2CoCl_4$ from 2200 to 3600 $cm.^{-1}$ (Perfluorokerosene mull).

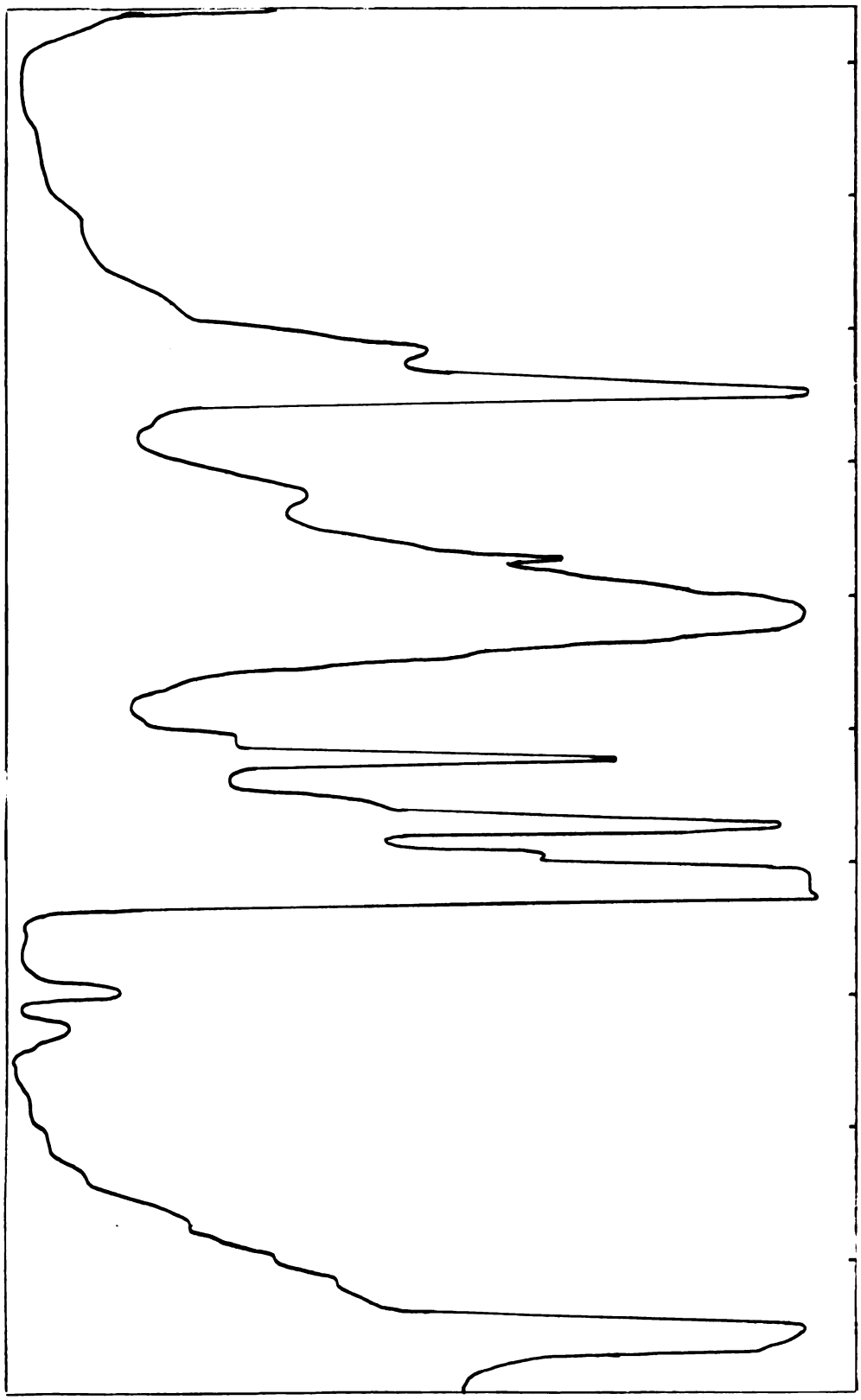


Figure 4. Infrared spectrum of $[(CH_3)_4]_2[Nb(OCH_3)Cl_5]$ (Nujol mull).

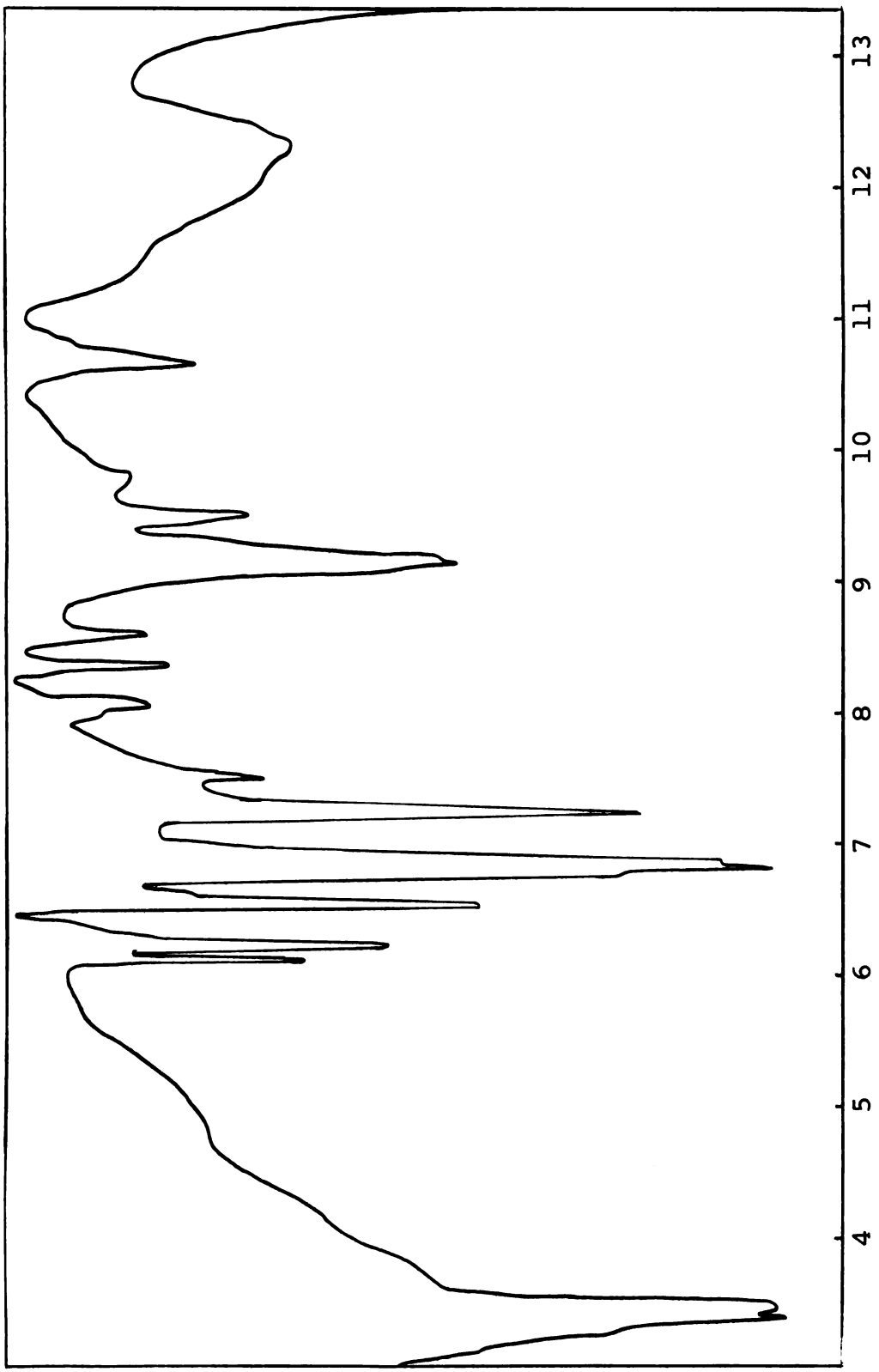


Figure 5. Infrared spectrum of $(C_5H_6N)_2[Nb(OCH_3)Cl_5]$ (Nujol mull).

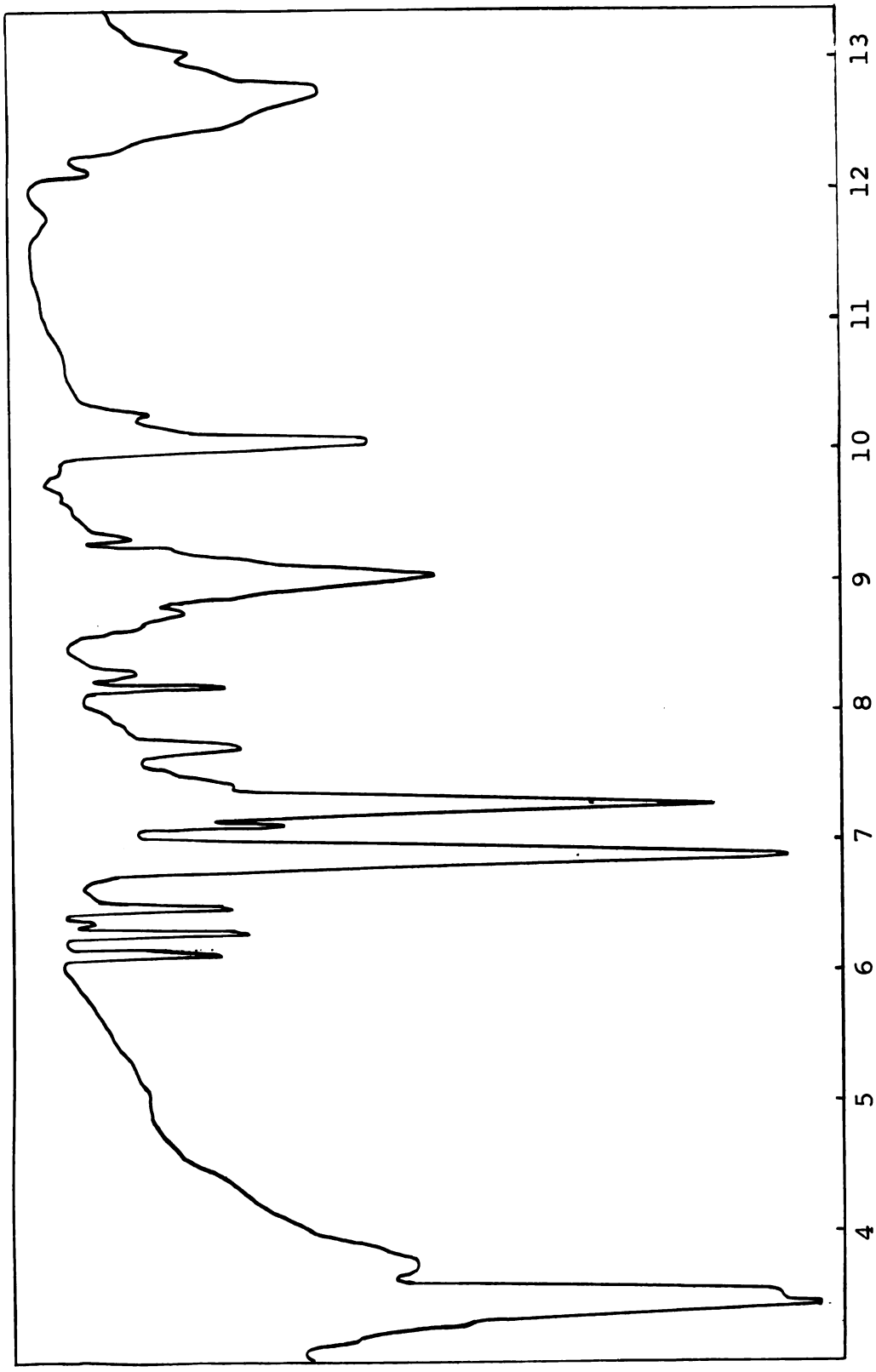


Figure 6. Infrared spectrum of $(C_9H_8N)_2[Nb(OCH_3)Cl_5]$ (Nujol mull).

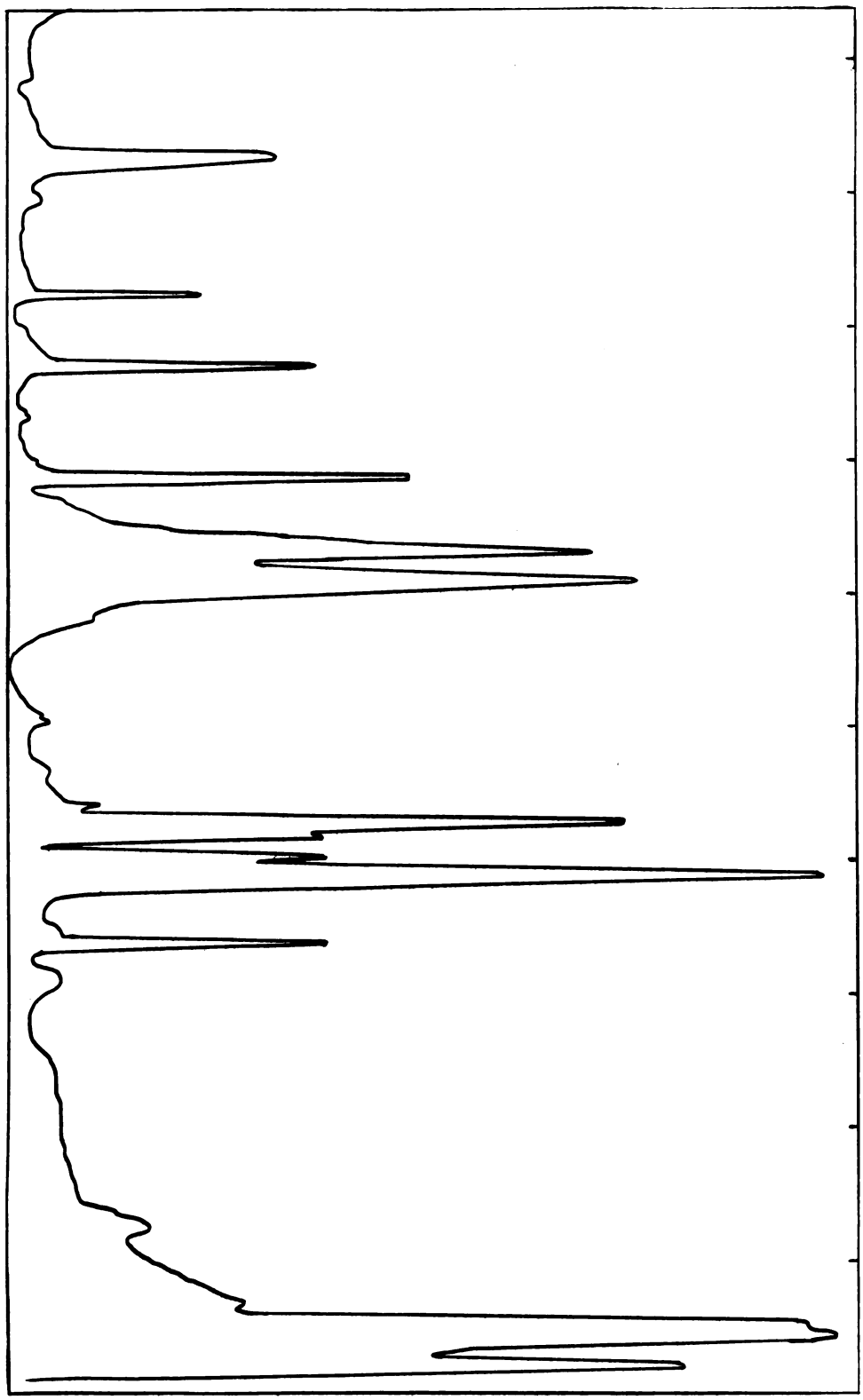


Figure 7. Infrared spectrum of $[(CH_3)_2NH_2]_2[Nb(OC_2H_5)Cl_5]$ (Nujol mull).

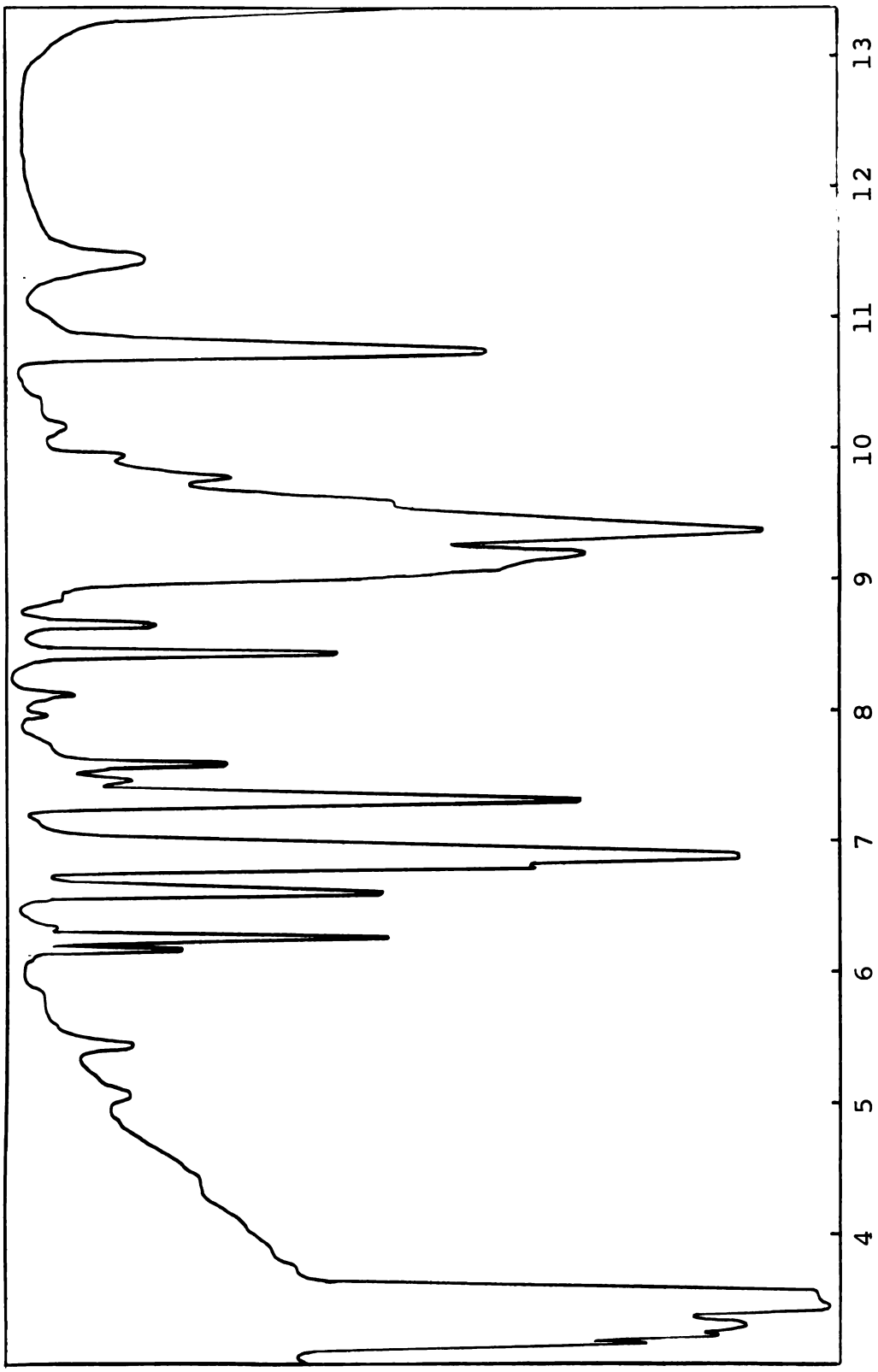


Figure 8. Infrared spectrum of $(C_5H_6N)_2[Nb(OC_2H_5)Cl_5]$ (Nujol mull).

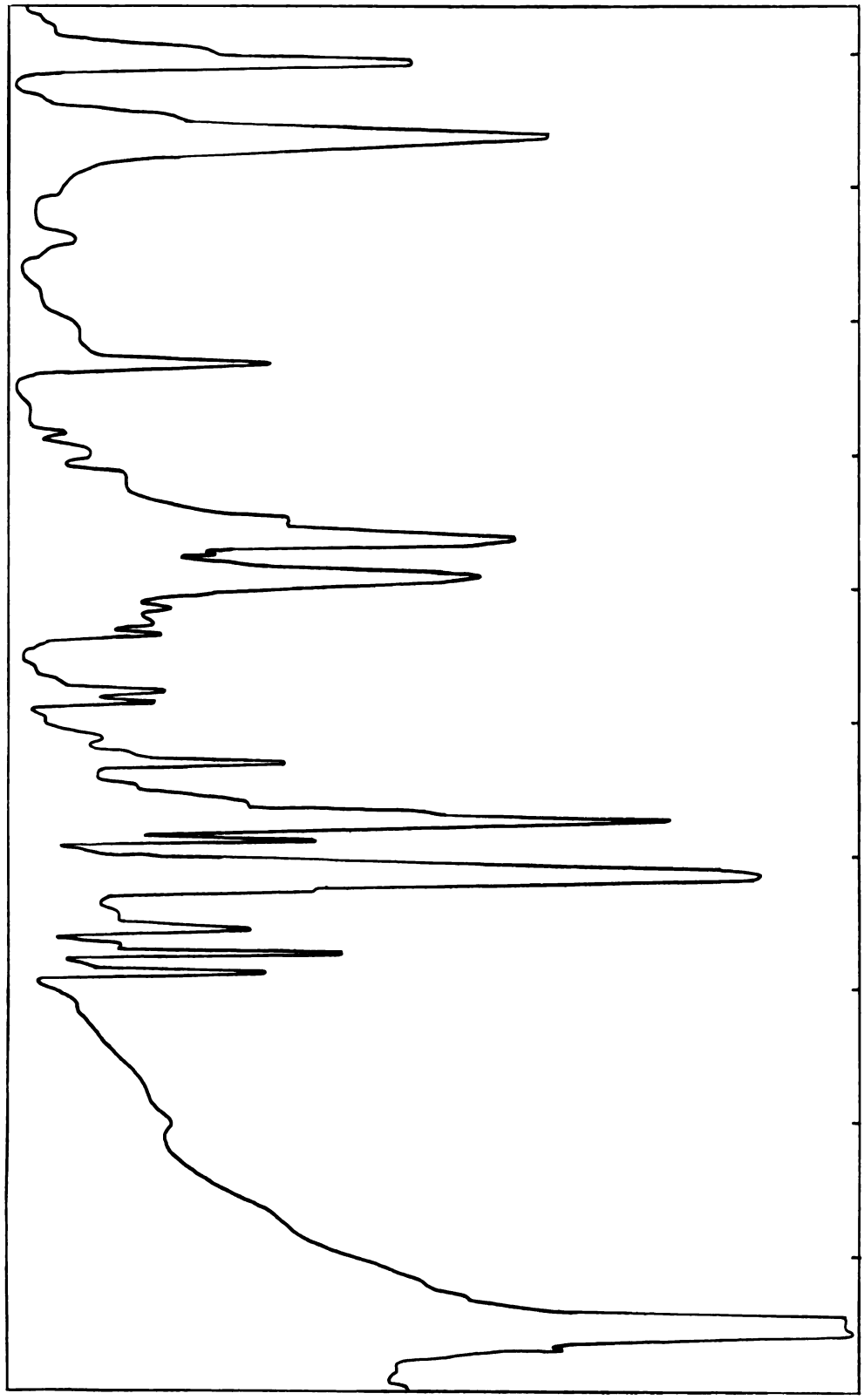


Figure 9. Infrared spectrum of $(C_9H_8N)_2[Nb(OC_2H_5)Cl_5]$ (Nujol mull).

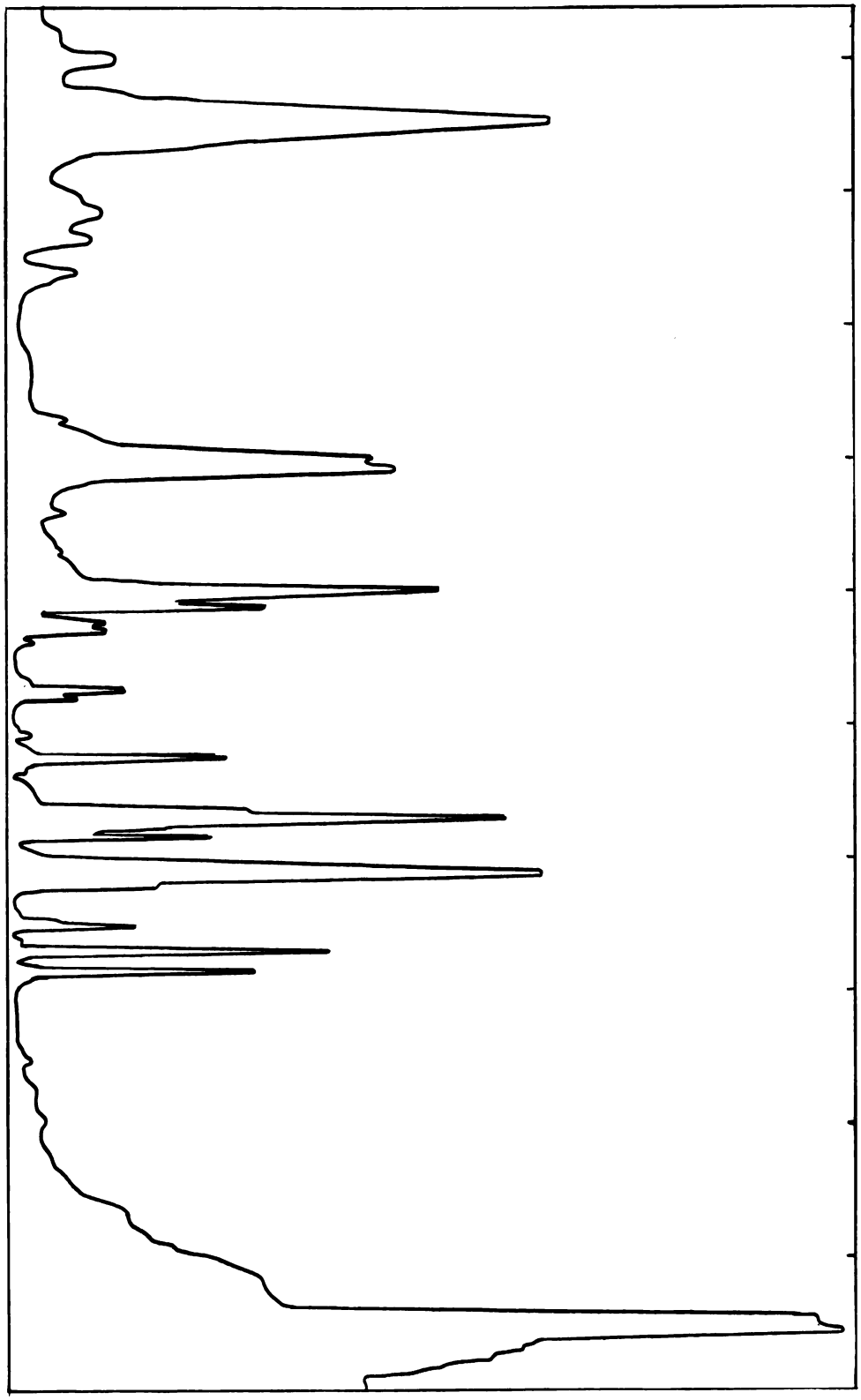
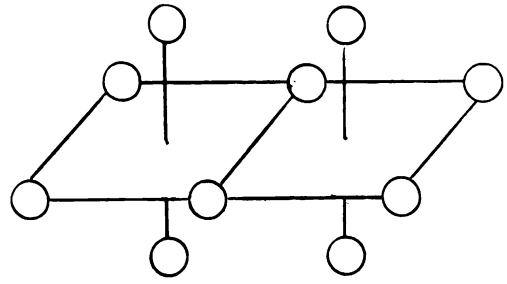


Figure 10. Infrared spectrum of $(C_9H_8N)_2[Nb(OC_3H_7)Cl_5]$ (Nujol mull).

$(C_9H_8N)_2[Nb(OCH_3)Cl_5]$, 1110 cm.$^{-1}$; $[(CH_3)_2NH_2]_2[Nb(OC_2H_5)Cl_5]$, 1070 and 1100 cm.$^{-1}$; $(C_5H_6N)_2[Nb(OC_2H_5)Cl_5]$, 1070 and 1090 cm.$^{-1}$; $(C_9H_8N)_2[Nb(OC_2H_5)Cl_5]$, 1070 and 1090 cm.$^{-1}$; and $(C_9H_8N)_2[Nb(OC_3H_7)Cl_5]$, 1030 and 1100 cm.$^{-1}$. A weakening C-O bond has occurred in the presence of pyridinium and quinolinium ions.

The ethoxo and isopropoxo compounds exhibit two absorptions 1000 and 1150 cm.$^{-1}$. Bradley[39] has noted a similar occurrence in the spectra of various ethoxides ($[Nb(OC_2H_5)_5]_2$, $[Ti(OC_2H_5)_4]_3$, etc.) and has concluded the cause to be the presence of both bridging and terminal alkoxide.



O represents the oxygen in ethoxide

The pentachloroalkoxoniobates can be pictured as monomeric and hexa-coordinated ions. But, if Bradley's conclusion is true, then polymeric structures containing both

bridged and terminal alkoxide must be imagined. This is a difficult task. Fortunately, such a process does not seem necessary when the spectra of ethyl alcohol and sodium ethoxide are considered. It seems likely that in either of these compounds all C-O bonds are equivalent; yet, both have two absorptions in the 1000-1150 $cm.^{-1}$ region.[40] Ethyl alcohol absorbs at 1055 and 1097 $cm.^{-1}$, while sodium ethoxide absorbs at 1062 and 1128 $cm.^{-1}$. Further assurance is had from the simplicity of the spectra of the pentachloromethoxoniobates which exhibit single maxima between 1090 and 1130 $cm.^{-1}$. Methyl alcohol and sodium methoxide behave similarly with absorptions at 1035 and 1074 $cm.^{-1}$ respectively. Thus, it seems reasonable to picture the complexes as monomeric, hexa-coordinated ions.

Some credence is lent to this picture from a consideration of the magnetic moments and the Curie-Weiss dependence of the susceptibilities of the complexes (Table I). This evidence, however, is not an absolute criterion for the mononuclear nature of the complexes. For example, Earnshaw and Lewis[41] have shown that magnetic interaction between two metal ions in a binuclear complex is sensitive to the nature of the bridging group and to the metal-ligand-metal bond angle. For $[(NH_3)_5Cr\text{-}OH\text{-}Cr(NH_3)_5]Br_5$, the magnetic

moment is very close to that for the free metal ion and the slight curvature in the plot of $1/X'_M$ against T is only detectible through precise measurements of the susceptibility at a considerable number of temperatures. For the seemingly similar compound, $[(NH_3)_5Cr\text{-}O\text{-}Cr(NH_3)_5]Br_4$, the moment deviates sharply from the free-ion value at low temperatures, and a pronounced antiferromagnetic interaction can be observed in the plot of $1/X'_M$ against T. This has been attributed to an increase in the metal-ligand-metal bond angle and a concurrent increase in π-bonding between the oxygen and the metal ions.

The evidence offered to this point is in accord with a monomeric, hexa-coordinated series of complexes. However, structurally, they cannot be this simple because the color of the complexes is dependent on the nature of the cation. Certainly, in most complexes, their color is due to d-d transitions within the metal ion, and should be little effected by the cation.

Reflectance spectra in the visible region were taken for a number of compounds (Figures 11 through 13). The simple alkylammonium methoxo and ethoxo salts show a single (very slightly asymmetric) band at about 19,600 $cm.^{-1}$ (510 mμ). The maxima in the spectra of the pyridinium

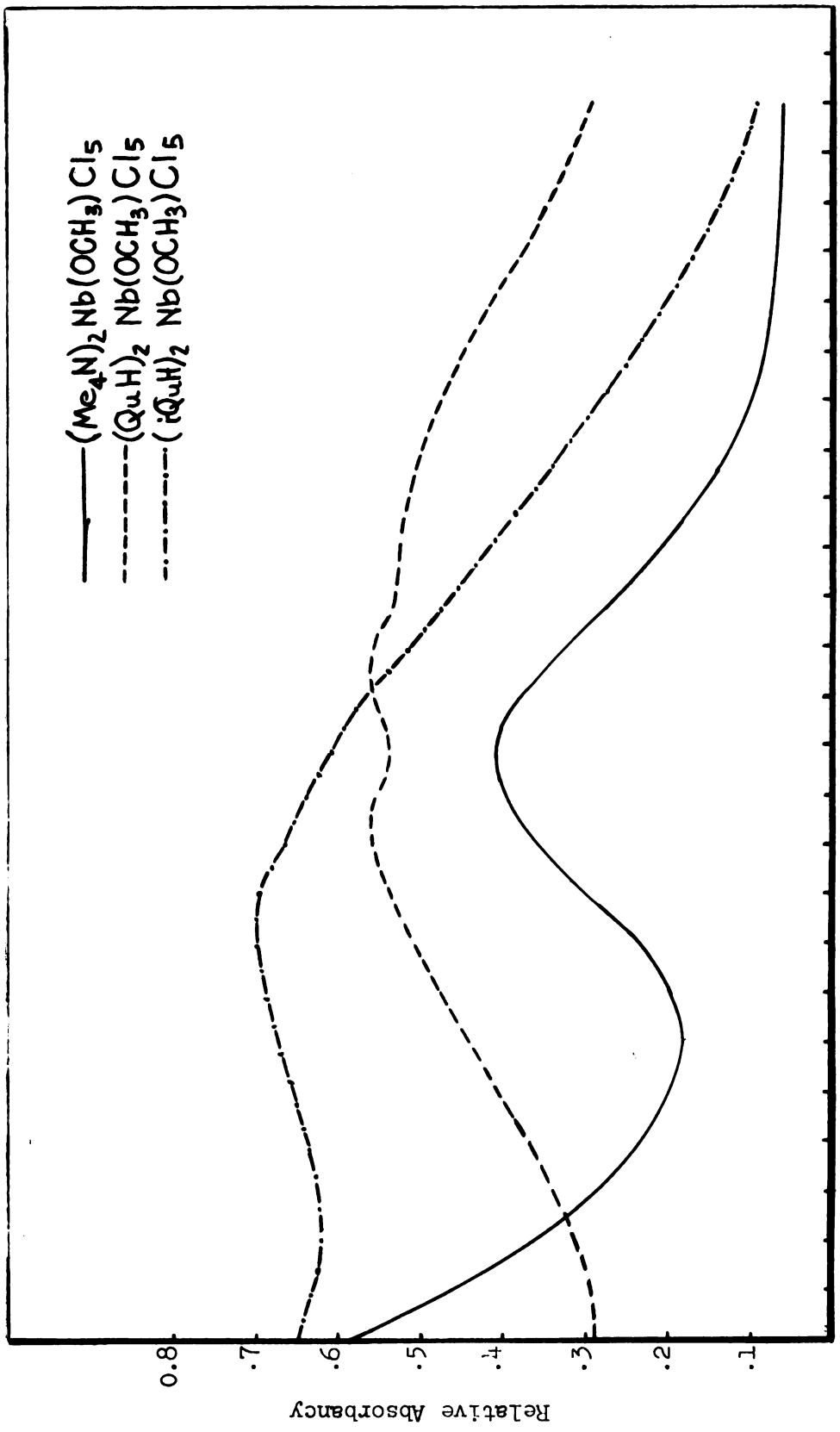


Figure 11. Visible reflectance spectra of some pentachloromethoxoniobates.

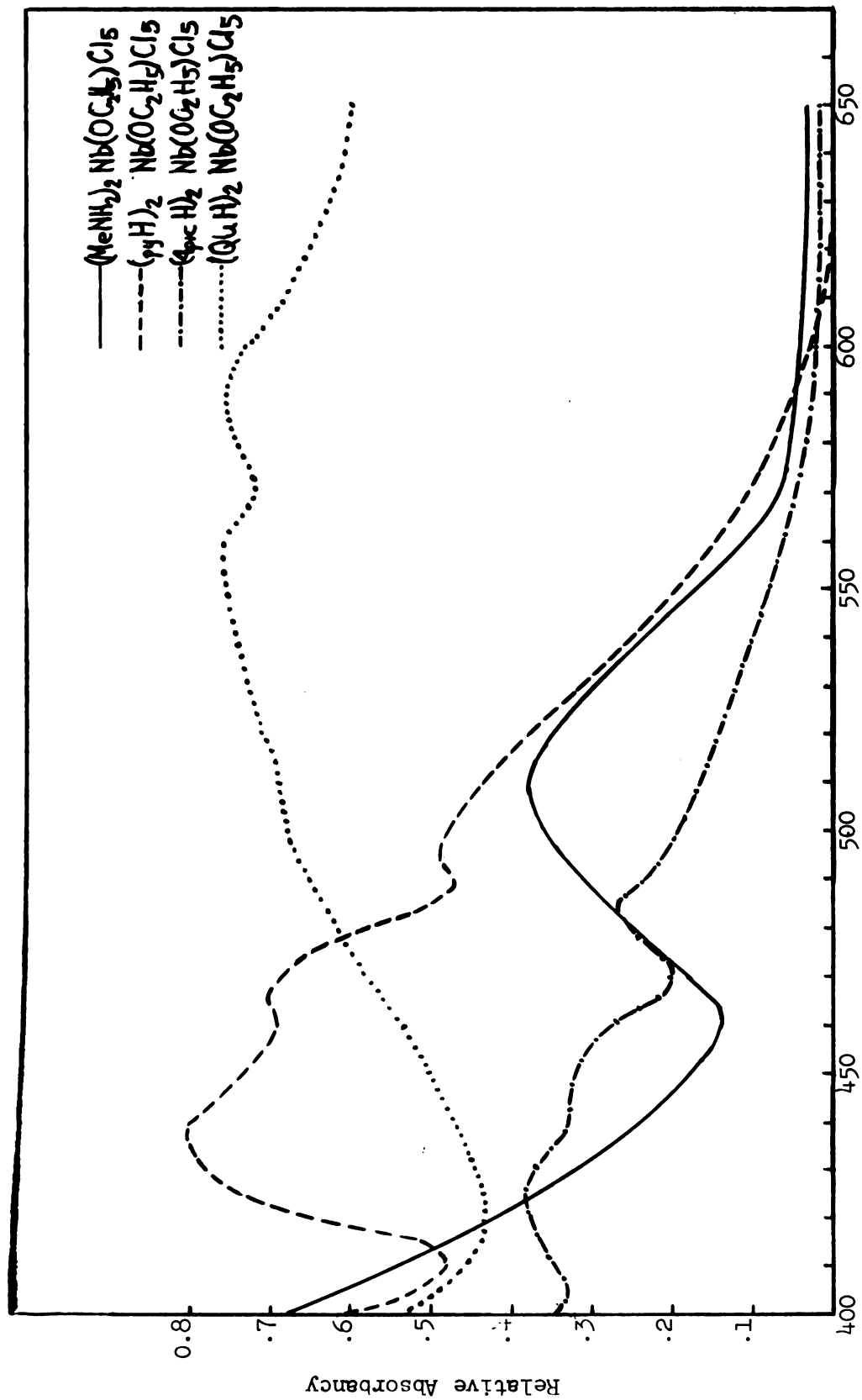


Figure 12. Visible reflectance spectra of some pentachloroethoxoniobates.

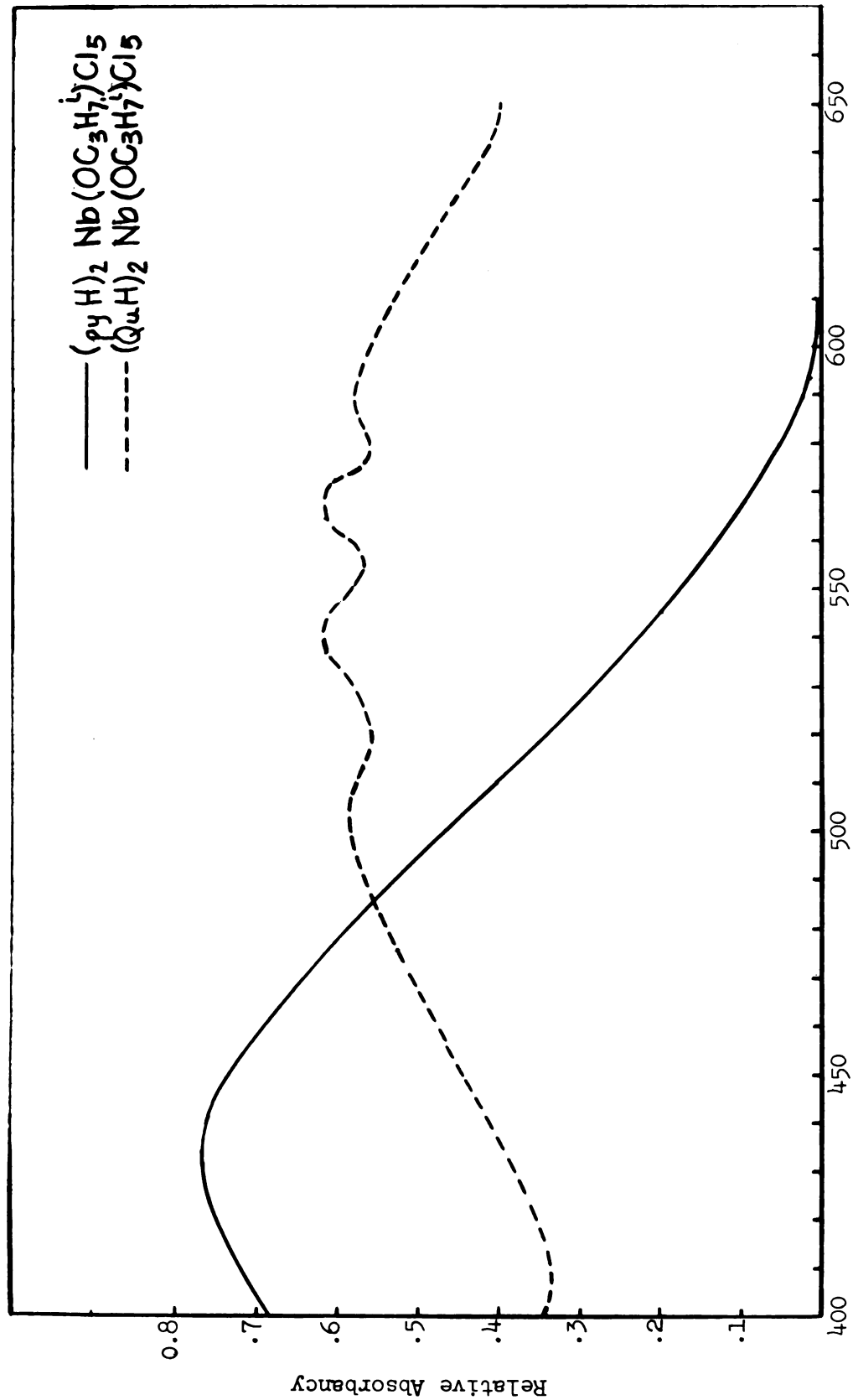


Figure 13. Visible reflectance spectra of some pentachloroisopropoxoniobates.

compounds are always shifted toward higher frequencies, and are considerably more asymmetric. The spectra of the quinolinium compounds are much more complex with a broad absorption band extending from 15,400 to about 22,100 $cm.^{-1}$. This band seemingly consists of two or three poorly resolved components. It is interesting to note that the spectra of the isoquinolinium pentachloromethoxoniobate(IV) does not resemble the quinolinium compound, but consists of an asymmetric band at 20,600 $cm.^{-1}$. No high intensity bands, such as might be associated with charge transfer, are present in any of the spectra, except at the limiting frequencies of these measurements for the ethoxo compounds.

The spectra of the alkylammonium compounds should be most readily interpreted, yet even in these there is considerable ambiguity in making spectral assignments. It seems reasonable to assume that these complexes are tetragonal; and that some π-bonding exists between the alkoxide oxygen and the metal ion. With these assumptions, the energy level diagram for the $[MoOCl_5]^{-2}$ ion[23] should be at least qualitatively useful in interpreting the spectra of the $[Nb(OR)Cl_5]^{-2}$ species; both of which possess C_{4v} symmetry.

a_1 (d_{z^2})

b_1 ($d_{x^2 - y^2}$)

e (d_{xz}, d_{yz})

b_2 (d_{xy})

The predicted transitions are $b_2 \longrightarrow e$, $b_2 \longrightarrow b_1$ (Δ), and $b_2 \longrightarrow a_1$. In the $[MoOCl_5]^{-2}$ ion the first two transitions occur at 13,800 and 23000 $cm.^{-1}$, respectively. The latter transition is apparently masked by a charge transfer band.

Due to limitations of the available spectrophotometer, the only observed transition for the alkylammonium compounds occurs at 19,600 $cm.^{-1}$. This might reasonably be assigned to either the $b_2 \longrightarrow e$ or $b_2 \longrightarrow b_1$ transitions; and, indeed, arguments for either can be presented.

Since the $b_2 \longrightarrow b_1$ transition in the $[MoOCl_5]^{-2}$ ion occurs at 23,000 $cm.^{-1}$, a value not too different from the observed transition, a similar assignment might be made for the $[Nb(OR)Cl_5]^{-2}$ ion.

In another approach, Jorgensen[42] argues that this transition can hardly be that of $b_2 \longrightarrow b_1$, because it would have about the same energy as Δ in the cubic complex $[NbCl_6]^{-2}$. This value is unknown at present; however, in

the complex $[MoCl_6]^{-3}$, Δ is 19,200 $cm.^{-1}$. Since the increased charge should introduce a 20% larger Δ, the value for $[NbCl_6]^{-2}$ should be about 23,000 $cm.^{-1}$. Since this is larger than that observed, the observed band must be due to the $b_2 \longrightarrow e$ transition.

The effect of the cation is not easily explained. The increasing complexity, without a great increase in intensity, in the visible region seems to argue that the tetragonal symmetry is even more distorted. The decrease in the C-O frequencies may mean that the interaction is weakening the C-O bond, while the decrease in the C-H frequency in the quinolinium cation provides a similar point of interaction. Perhaps, then, the aromatic protonated bases are interacting with the complex, possibly through the alkoxo-group oxygen, and providing even more distortion of the complex.

This explanation is open to doubt also, since the vibrational frequencies characteristic of the pyridinium and quinolinium ring systems (Table 2 and 3) are certainly not greatly altered, if any, from those of the simple hydrochlorides.

At this point it does not even seem possible to say that exact structural determination must await X-ray

examination because decomposition of the samples occurs when they are irradiated with X-rays.

The spectra of the solutions from above the precipitated solid complexes are not similar to those of the solids, indicating that the species in solution is not the same as that in the solid complex. However, the spectra from all the supernatant solutions are almost identical, with a single maxima at 21,300 $cm.^{-1}$ in the region from 14,300 to 25,000 $cm.^{-1}$. Therefore, for a given alcohol, the species in solution, whatever its nature, is independent of the nature of the cation.

Another feature of the pentachloroalkoxoniobates that is worthy of note is their stability towards hydrolysis. Since fairly good yields of the pyridinium ethoxo compound were isolated from 90% ethyl alcohol solutions, it is obvious that careful drying of the solvent is not necessary for preparative purposes. Ordinary laboratory absolute alcohol is sufficient to guarantee good yields of the complexes.

The stability of the alkoxo-niobium bond toward hydrolysis may seem anomolous, but it would seem to support the contention that π-bonding exists between the alkoxo-group oxygen and the metal ion. This would tend to make oxygen's ordinarily non-bonding electrons unavailable for

protonation (a step which could logically precede a dissociative S_N1 release of the alkoxo group), and strengthen the niobium-oxygen bond. Jorgensen[43] has commented on the stability of the oxo-group in VO^{+2} and MoO^{+3} toward protonation, even in solutions of high acidity, and has correlated this property with extensive π-bonding between the oxygen and the metal ion.

Dichlorohexaethoxobis(pyridine)diniobium(IV)

This interesting dimeric compound possesses so many non-equivalent ligands that an accurate structural determination based on chemical and physical properties alone is impossible. Inspection shows there are forty-three possible isomers based on the following assumptions.

1. Each niobium is octahedrally surrounded by ligands.
2. Each niobium is maintained in the tetravalent state, i.e., a niobium(III)-niobium(V) combination is not allowed.
3. Pyridine cannot act as a bridging ligand, but any other combination of bridging ligands is possible.

The infrared spectrum (Figure 14) makes it clear that ligand pyridine is present, since the strong absorption characteristic of pyridinium ion at 1630 $cm.^{-1}$ is absent.

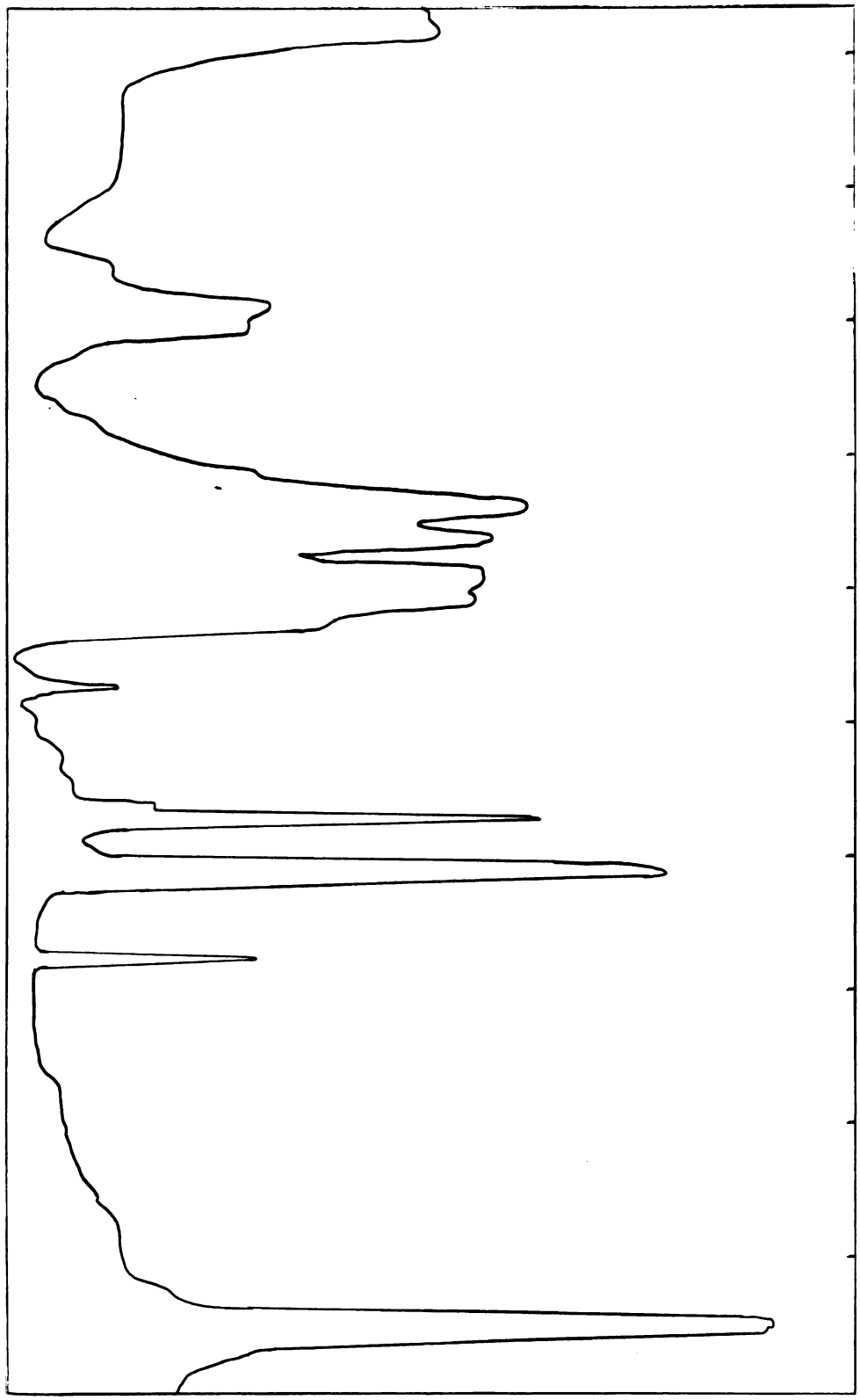
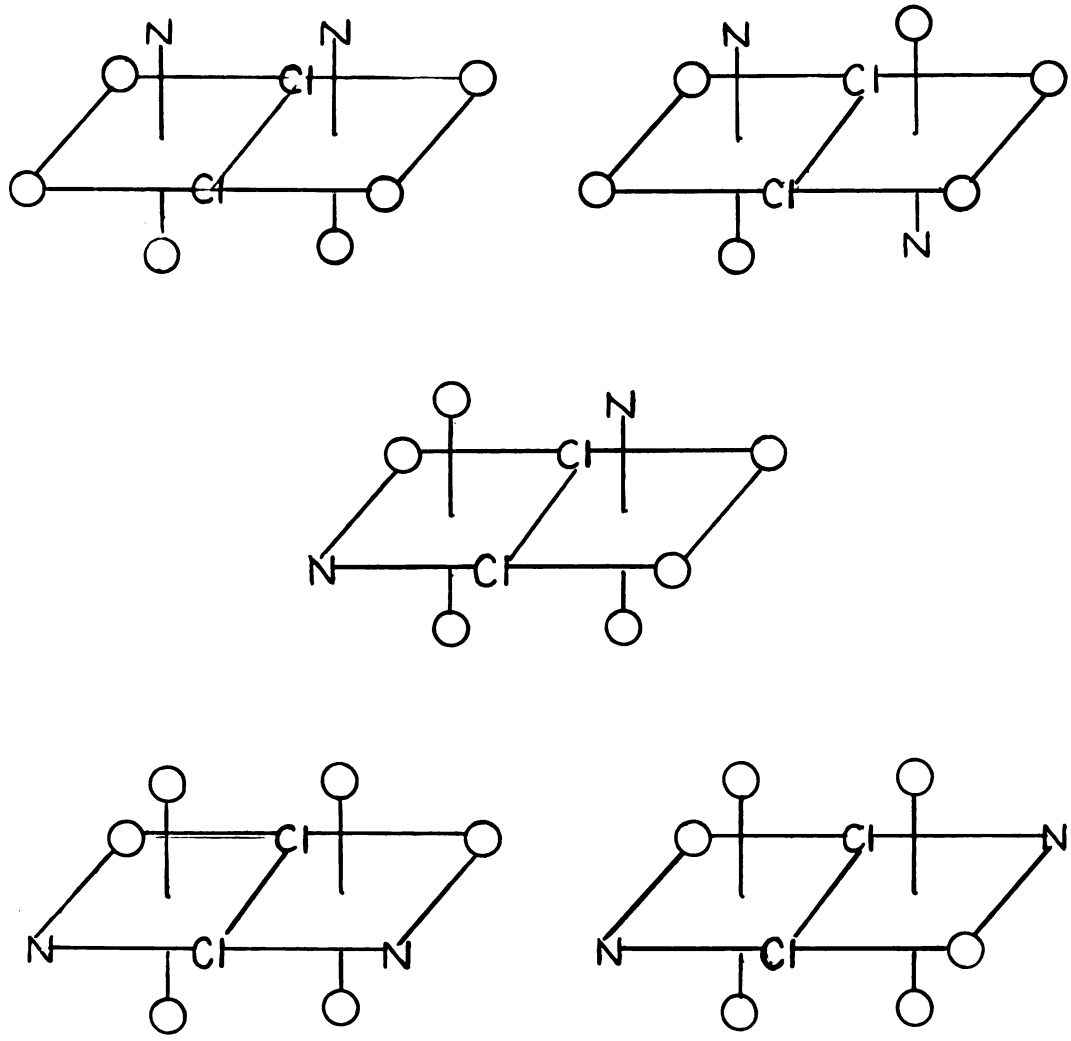


Figure 14. Infrared spectrum of $[NbCl(OC_2H_5)_3(C_5H_5N)]_2$ (Nujol mull).

The region of the spectrum, in which the characteristic C-O absorptions occur (ca. 1100 $cm.^{-1}$), is quite complex. Exact frequencies are 1010 m, 1040 s, 1000 s, 1120 s (shoulder), and 1140 $cm.^{-1}$ m. This is certainly evidence for non-equivalent alkoxo groups. Moreover, it could be interpreted as evidence for bridging and terminal alkoxo groups.

The inability to replace chloride ion by solvolysis and precipitation as KCl, however, points to the inertness of this ligand. In the kinetically-stable $[Co(NH_3)_5Cl]^{+2}$ and $[Pt(NH_3)_3Cl]^{+}$ ions the chlorides are fairly readily replaced. It is only in certain dimeric palladium and platinum complexes which possess chloride bridging that kinetic inertness of the chloride ion is encountered. It seems logical then to assume that in the dimeric niobium compound the chloride ions are bridging groups. With this assumption the number of isomers is reduced to five (Figure 15).

If this is the case, how can the complexity of the infrared spectrum between 1000 and 1100 $cm.^{-1}$ be explained? In the structures shown in Figure 15, all of the oxygens are not really equivalent, since some are trans to pyridine, while others are trans to chloride or oxygen. A non-equivalence



O represents oxygen in ethoxide.
N represents nitrogen in pyridine.

Figure 15. Isomers of $[NbCl(OC_2H_5)_3(C_5H_5N)]_2$ with chloride bridging.

π-bonding between the oxygens and the metal ion, resulting from differing trans groups, could greatly effect the C-O absorption spectrum, and cause the observed complexity.

The observed diamagnetism does not afford any additional evidence concerning the nature of the bridging groups, but it does provide a stimulus for investigating the nature of the spin-pairing mechanism. In NbI_4 (see Introduction) the diamagnetism is explained by direct metal-metal bonding because the metal-metal distance is only 3.3 Å. Using the covalent radius for niobium of 1.3 Å and assuming the bridged chloride to have a slightly larger radius than the covalent radius of 0.99 Å[44] (say 1.1 Å), then simple trigonometry allows a calculation of 3.5 Å for the niobium-niobium intramolecular distance. This seems to agree well enough with that observed in NbI_4 to postulate that the spin-pairing occurs by direct overlap of the adjacent metal d_{xy} orbitals. If the niobium ions are shifted from the centers of their octahedra toward each other, as is observed in NbI_4, then overlap would be even more favorable.

The visible and near-infrared spectrum of the dimer in $CHCl_3$ and ethyl alcohol is particularly uninformative, consisting only of a shoulder at about 27,400 $cm.^{-1}$ adjacent

to a large charge transfer band in the ultraviolet region. The molar extinction coefficient at 27,400 $cm.^{-1}$ using three separate solutions was 190, 310, and 520 $l.\ mole^{-1}\ cm.^{-1}$. Any of these values are anomolously high for a d-d transition in an octahedral complex. The lack of agreement and the high values can probably be attributed to oxidation.

Tetraethoxoniobium(IV)

Prompted by Bradley's numerous successful preparations of tetravalent metal alkoxides (for example, Ti(IV), Zr(IV),[46] Hf(IV),[47] Ce(IV),[48] Th(IV),[49] Sn(IV),[50] and V(IV)[52]) and by the successful preparation of several chloro-alkoxo niobium(IV) species during this research, the preparation of tetraethoxoniobium(IV) was attempted.

Bradley has used three general methods for the preparation of metal alkoxides:

1. The Ammonia Method:

$$MCl_4 + 4ROH + 4NH_3 \longrightarrow M(OR)_4 + 4NH_4Cl\downarrow$$

This method was applied with success to Ti(IV), Zr(IV), and Hf(IV). For Ce(IV), which does not form a stable tetrachloride, the compound $(C_5H_6N)_2CeCl_6$ was used instead.

$$(C_5H_6N)_2CeCl_6 + 6NH_3 + 4ROH \longrightarrow Ce(OR)_4 + 6NH_4Cl\downarrow + 2\ C_5H_5N$$

2. The Sodium Alkoxide Method:

$$MCl_4 + 4\ NaOR \longrightarrow M(OR)_4 + 4\ NaCl\downarrow$$

With $SnCl_4$, the ammonia method did not result in complete precipitation of the chloride as ammonium chloride. Moreover, attempts to prepare thorium alkoxides by a similar method were also unsuccessful. However, the use of sodium alkoxide resulted in the complete removal of chloride.

3. The Solvolytic Method:

With VCl_4, neither of the above methods were successful, but solvolysis of tetrakis(dialkylamido)vanadium(IV) with alcohol produced the desired alkoxide.

$$M(NR_2)_4 + 4\ ROH \longrightarrow M(OR)_4 + 4\ R_2NH$$

Thomas, however, was not able to apply this method successfully to niobium(IV) because of oxidation to $Nb(OR)_5$.[51] He has attributed the lack of success to the instability of the tetralkoxide in the presence of alcohol, presumably:

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

In this research, the ammonia method was not successful, but the sodium alkoxide method, when applied to $[NbCl(OC_2H_5)_3(C_5H_5N)]_2$, produced the desired $Nb(OC_2H_5)_4$ with no apparent oxidation.

$$[NbCl(OC_2H_5)_3(C_5H_5N)]_2 + 2\ NaOC_2H_5 \longrightarrow$$

$$2\ Nb(OC_2H_5)_4 + 2\ NaCl + 2\ C_5H_5N$$

The niobium alkoxide is readily purified by sublimation. Volatility is quite common among the alkoxides of metals of low atomic number as the following table illustrates:

Table IV. Boiling or sublimation temperatures of metal ethoxides (in °C/mm. Hg.).

$Ti(OC_2H_5)_4$	103/0.1[46]
$Zr(OC_2H_5)_4$	180*/0.1[46]
$Hf(OC_2H_5)_4$	180-200*/0.1[47]
$Ce(OC_2H_5)_4$	non-volatile[48]
$Th(OC_2H_5)_4$	non-volatile[49]

*Sublimed.

Another feature of the metal alkoxides is their tendency to polymerize. Molecular weight studies on the niobium compound were not attempted, however, because of the limited amounts of pure material available and its extreme sensitivity to oxidation and hydrolysis. The diamagnetism of an impure sample suggests that the niobium

compound is also polymeric.

The infrared spectrum (Figure 16) in the C-O vibrational region is only slightly more complex than the pentachloroethoxoniobates: 1030 m (shoulder), 1040 s (shoulder), 1060 s, 1100 s, and 1140 cm.$^{-1}$ s (shoulder). Since the evidence points to a polymer, then the molecule must consist of both bridging and terminal ethoxides. Yet, the spectrum is relatively simple. This simplicity might support the postulate that the complexity of the spectrum of $[NbCl(OC_2H_5)_3(C_5H_5N)]_2$ is due to a trans effect, rather than a difference due to bridging and terminal ethoxides.

The visible and near-infrared spectrum of $Nb(OC_2H_5)_4$ in ethyl alcohol is almost identical to that of $[NbCl(OC_2H_5)_3(C_5H_5N)]_2$ with only a shoulder at about 27,800 cm.$^{-1}$ (ϵ = 20 l. mole^{-1} cm.$^{-1}$).

Both $Nb(OC_2H_5)_4$ and $[NbCl(OC_2H_5)_3(C_5H_5N)]_2$ are extremely labile to chloride substitution and depolymerization in solutions of strong acidity. Lability is to be expected for d^1 metal ions,[52] but the ease of depolymerization is somewhat surprising. This feature has enabled an interesting cycle of reactions to be completed:

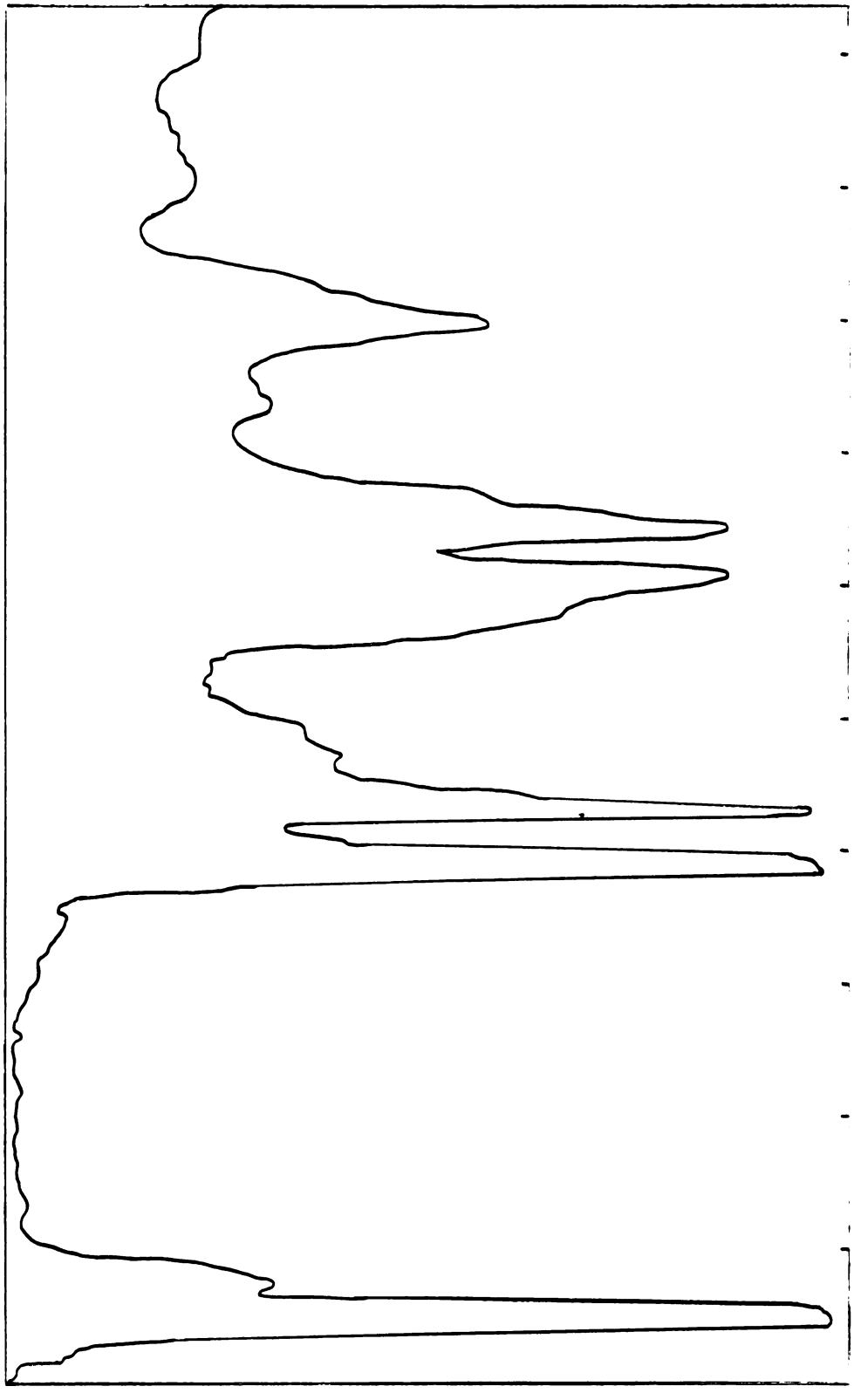
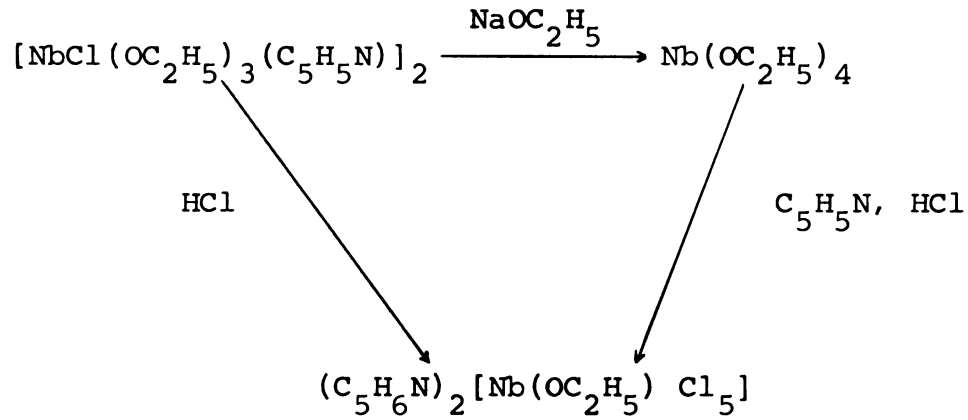


Figure 16. Infrared Spectrum of $Nb(OC_2H_5)_4$ (Nujol mull).



Since the pentachloroethoxoniobate can be prepared from either of the two species, they must be niobium(IV) derivatives and not an equimolar combination of niobium(III) and niobium(V).

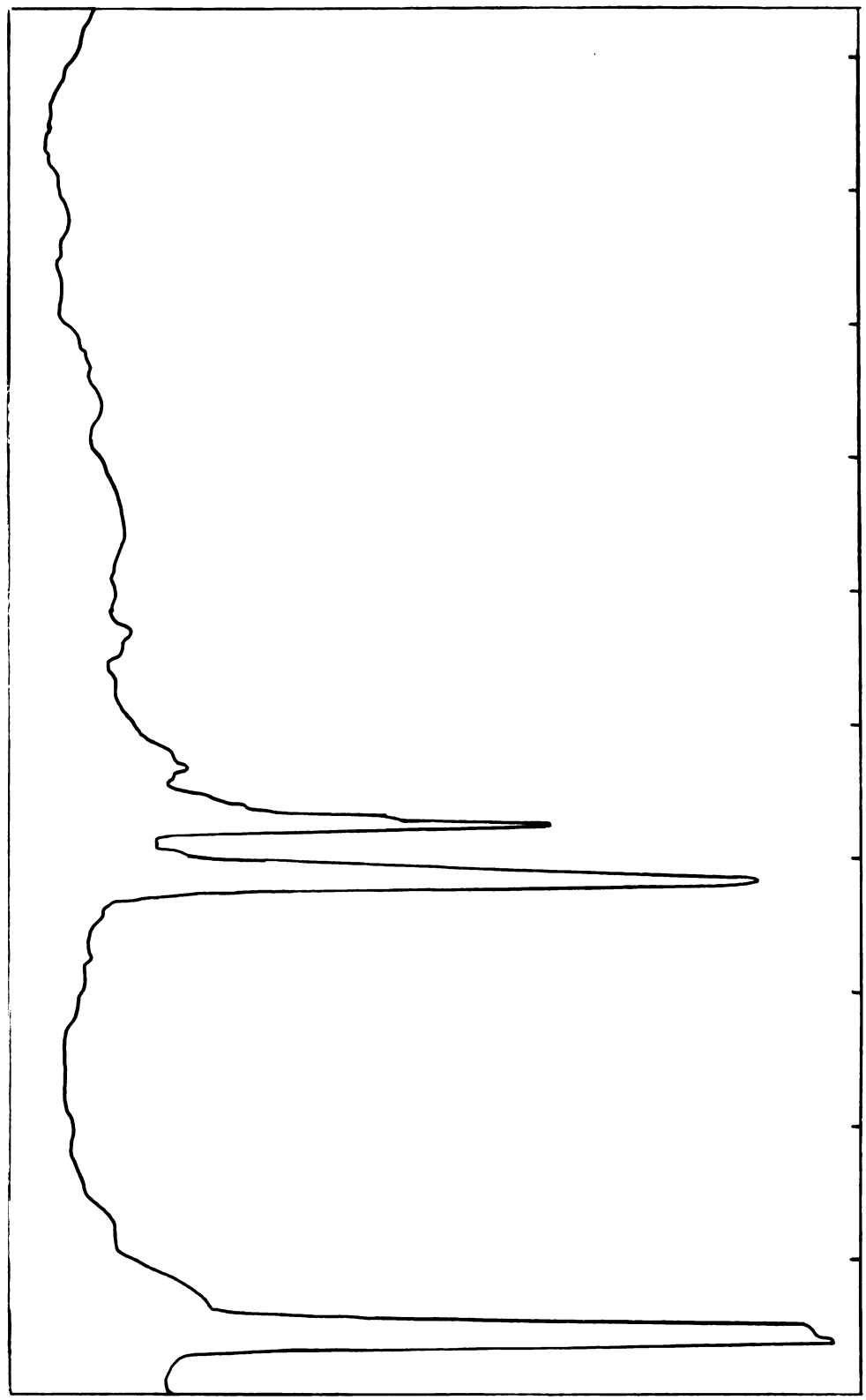


Figure 17. Infrared spectrum of Nujol.

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