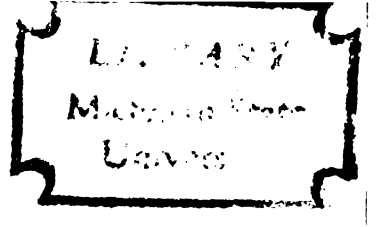


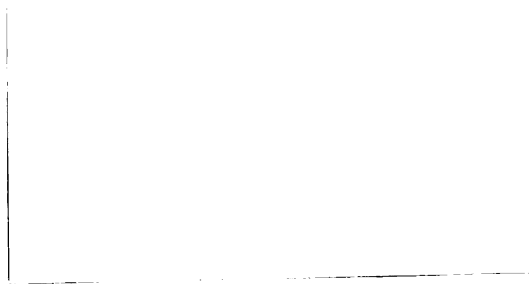
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THE PREPARATION OF SOME
TRANSITION METAL ALKOXIDES

Thesis for the Degree of M. S.
MICHIGAN STATE UNIVERSITY
Mark Wicholas
1964



MICHIGAN STATE UNIVERSITY
DEPARTMENT OF CHEMISTRY
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ABSTRACT

THE PREPARATION OF SOME TRANSITION METAL ALKOXIDES

by Mark Wicholas

Four alkoxides and chloroalkoxides of copper (II) have been prepared and characterized. The alkoxides, $\text{Cu}(\text{OCH}_3)_2$ and $\text{Cu}(\text{OC}_2\text{H}_5)_2$ were prepared by reaction of stoichiometric quantities of the appropriate lithium alkoxides and copper (II) chloride in alcohol. The chloride alkoxides were also prepared by reaction of stoichiometric quantities of the appropriate lithium alkoxide and copper (II) alkoxide in alcohol and by reaction of copper (II) chloride and the copper (II) alkoxides in alcohol.

The alkoxides are insoluble in all common solvents whereas $\text{Cu}(\text{OCH}_3)\text{Cl}$ is soluble in acetone and $\text{Cu}(\text{OC}_2\text{H}_5)\text{Cl}$ in 3-pentanone--both with possible solvolysis. The infrared spectra of these and other alkoxides show that bridging alkoxide groups, terminal alkoxide groups or both can be detected by the position of the C-O absorption band. For the copper (II) alkoxides both bridging and terminal groups are judged to be present, whereas only bridging groups are present in the chloride alkoxides.

$\text{Cu}(\text{OCH}_3)_2$ and $\text{Cu}(\text{OC}_2\text{H}_5)_2$ and $\text{Cu}(\text{OC}_2\text{H}_5)\text{Cl}$ each exhibit two bands in their visible spectra whereas $\text{Cu}(\text{OCH}_3)\text{Cl}$ shows only one band. The number of bands are taken as evidence that there is a reduction of symmetry from octahedral to tetragonal. The position of the bands is consistent with the spectrochemical series in that chloride is a weaker ligand than ligands bound through oxygen, since absorption in the alkoxides is at higher energy than in the chloride alkoxides.

Mark Wicholas

The magnetic susceptibilities of the alkoxides and chloride alkoxides are found to be much lower than 1.72 B.M., the spin-only moment. The magnetic moments of the chloride alkoxides are found to be higher than those of the alkoxides. The spin pairing can be caused by either a superexchange mechanism or by direct overlap of d orbitals of two copper (II) ions.

The structure suggested for both the alkoxides and chloride alkoxides is a three dimensional polymer consisting of copper atoms bonded in an tetragonal environment.

Investigation of mixed metal alkoxides resulted in the synthesis of iron (III) phenoxide. Attempts to produce double alkoxides of thallium (I) and iron (III), cobalt (II) and titanium (IV), and iron (II) and titanium (IV) were all unsuccessful.

THE PREPARATION OF SOME TRANSITION METAL ALKOXIDES

By

Mark Wicholas

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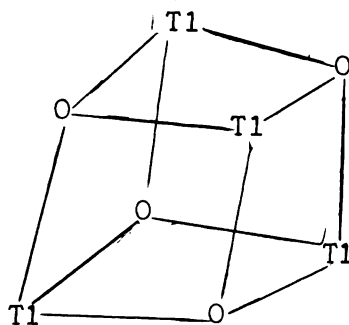
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INTRODUCTION

Metal alkoxide compounds have been known for over a century; however, very little has been ascertained about their properties and structures.

Much investigation has been done concerning the reaction of alkoxides, particularly those of Na, K, Mg, Ca, Al, and Ti in organic systems. Review articles of this and other alkoxide chemistry have been written by Bradley (1,2,3).

Some transition metals have been reported to form alkoxides. Most investigated have been found to be covalent, volatile, polymeric substances where the degree of polymerization varies from two to eight. There have been no complete x-ray structure determinations for any of the transition metal alkoxides. Only one structure determination has been reported -- that of TiOCH_3 (4), which is tetrameric and is of a distorted cubic symmetry as shown. A structural theory has been advanced by Bradley (5)



Thallous Ethoxide

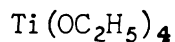
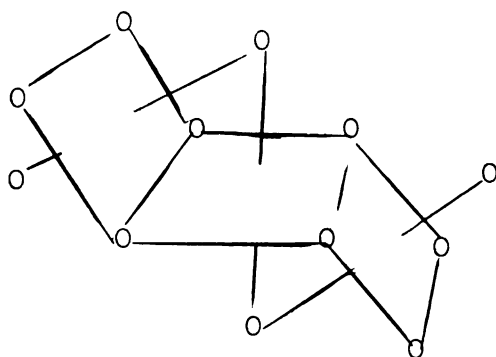
O = oxygen in ethoxide

and is based on hydrolysis experiments with titanium alkoxides and from molecular weight studies (ebulliometry and cryoscopy).

The transition metal alkoxides of groups 4B and 5B have been most extensively studied because of their covalency, volatility, and solubility

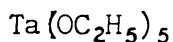
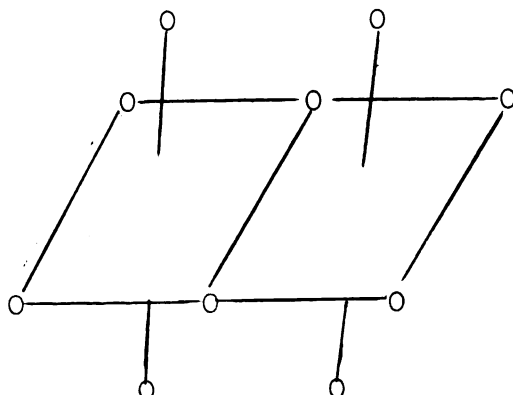
in organic solvents. Tetraalkoxides of titanium were first prepared in 1875 (6), and since then the following physical constants have been determined: degree of polymerization, volatility, heat and entropy of vaporization, density, viscosity, parachor, dipole moments, and refractivities. Reference to these can be found in Bradley's review article(3). The alkoxides of the congeners zirconium (7) and hafnium (8) have also been synthesized, but have been less thoroughly studied. Similar research has been done with the group 5B pentaalkoxides of niobium (9) and tantalum (10), which were investigated by Bradley. Vanadium pentaalkoxides have not yet been synthesized probably because of steric factors.

Caughlan (11) has found that the group 4B tetraalkoxides have a maximum degree of polymerization equal to three and proposes that the molecules consist of three interpenetrating octahedra as shown below:



O = oxygen in ethoxide

For group 5B, the maximum degree of polymerization is two for the pentaalkoxides, and he proposes a structure of two alkoxide bridged octahedra(10) as shown below:



O = oxygen in ethoxide

In the latter group, alkoxides have been synthesized where the metal is of a lower oxidation state. More specifically, Bradley has reported the existence of vanadium tetraalkoxides (12) and trialkoxides (13). The degree of polymerization of $\text{V}(\text{OCH}_3)_4$ is 2.79 or almost three. The trialkoxides are solids insoluble in organic solvents, and hence no physical properties were reported. Brubaker and Wentworth (14) have prepared the extremely unstable $\text{Nb}(\text{OC}_2\text{H}_5)_4$ which is diamagnetic and so possibly dimeric.

$\text{Cr}(\text{OC}_2\text{H}_5)_3$ (15) and $\text{Mn}(\text{OC}_2\text{H}_5)_2$ (16) and their alcoholates are also known. Unique alkoxides of tetravalent chromium have only recently been reported (17), and these d^2 compounds are paramagnetic, $\mu_{\text{eff}} = 2.79 - 2.82$ B.M.

Ferric alkoxides were first made in 1930 (18) and are known to be trimeric (19) and volatile under reduced pressure.

Barracough (20) has recorded the infrared spectra of many of the transition metal alkoxides and has made assignments to the metal-oxygen and carbon-oxygen stretching frequencies.

Some lanthanide metal alkoxides have been synthesized. Mehotra (21) has prepared simple trialkoxides of La, Pr, and Nd, which are all monomeric. Bradley (22) has investigated the covalent alkoxides of Ce(IV). The primary alkoxides are polymeric solids which are volatile at high temperatures and reduced pressures, whereas the tertiary alkoxides are liquid monomers.

Both Bradley and H. Gilman have investigated actinide metal alkoxides. Bradley has synthesized the covalent polymeric thorium tetraalkoxides, of which the maximum degree of polymerization is six, and plutonium tetraalkoxides (24). Alkoxides for the following uranium species are known: U(IV) (25), U(V) (26), and U(VI) (both $U(OR)_6$ and $UO_2(OR)_2$ (27,28)). As most metal alkoxides these show considerable volatility and covalency. Many novel synthetic routes were used for the preparation of the U(V) and U(VI) alkoxides.

Of interest also are the double or mixed metal alkoxides, which involve transition, actinide, or lanthanide elements. The compounds can be represented as $MM'(OR)_x$ where M, M', or both are either transition, lanthanide, or actinide elements. These compounds should contain bridging alkoxide groups between the different metals, which might then allow electron super-exchange across the bridge.

Meerwein first synthesized double alkoxides in 1929 (29), but of the more than 50 reported by him, only six contained transition elements, and half of these compounds have since been disproven (30). The remaining three were formed by the reaction of $NaAl(OC_2H_5)_4$ with $CuCl_2$, $NiCl_2$, and $CoCl_2$ respectively. Bartley and Wardlaw (30) have prepared a series of double alkoxides of zirconium, $MZr_2(OR)_9$, where M is Li, Na, or K. Most were found to be monomeric.

Albers (31) reported the preparation of the uranium aluminum isopropoxide $UAl_4(OC_3H_7)_6$. Further work by Gilman (32), showed that $U(OC_2H_5)_5$ would readily form double alkoxides as $NaU(OC_2H_5)_6$, but that $U(OC_2H_5)_4$ would not.

EXPERIMENTAL

Materials

All chemicals used in this investigation were of reagent grade unless otherwise stated. All solvents were dehydrated before using. Methanol and ethanol were refluxed with magnesium shavings and were then distilled, whereas, isopropanol was refluxed with calcium turnings and was then distilled. Benzene was refluxed with phosphorous pentoxide and distilled.

Preparation of Metal Alkoxides

Aluminum Isopropoxide was prepared from aluminum foil and dry isopropanol according to the method of Wilds (33).

Thallium (I) Ethoxide was prepared according to West (4) from thallium metal (K & K Laboratories - 99.8%), absolute ethanol, and oxygen. The infrared spectrum is presented in Figure 1 and agrees with that published by West.

Thallium (I) Phenoxide was prepared by the procedure of Menzies and Christie (34), from thallium (I) ethoxide and phenol. The infrared spectrum is presented in Figure 2.

Iron (III) Ethoxide was prepared by a method similar to that of Thiessen (18). Anhydrous ferric chloride was added to an ethanol solution of sodium ethoxide. After refluxing for an hour, the solvent was removed under reduced pressure, and the residue was extracted with benzene. Iron (III) ethoxide was isolated from this solution. The

infrared spectrum is presented in Figure 3.

Titanium Isopropoxide was kindly donated by P. Dupree and was Anderson, practical grade.

Preparation of Metal Halides

Uranium (IV) Chloride. $\text{UO}_4 \cdot x\text{H}_2\text{O}$ was first prepared from uranyl nitrate hexahydrate and 3% hydrogen peroxide (35). The dried product was then heated in an oven at 250°C for four hours to yield uranium trioxide. Following Hermann's procedure (36), uranium (IV) chloride was made from the trioxide and hexachloropropylene (Aldrich Chemical Co.).

Cobalt (II) Chloride. The anhydrous salt was prepared by dehydrating the hexahydrate by refluxing with thionyl chloride as described by Prey (37).

Copper (II) Chloride was prepared similarly to CoCl_2 .

Iron (II) Chloride was synthesized from anhydrous ferric chloride and chlorobenzene (38).

Analytical Methods

Iron Analysis. Fe(III) in $\text{Fe(OC}_6\text{H}_5)_3$ was determined by ignition of the sample to Fe_2O_3 . In the Fe(III) , Tl(I) mixtures, the samples were first hydrolyzed in dilute HCl , and the TlCl was filtered from the Fe(III) filtrate. After addition of potassium iodide, the liberated iodine was titrated with standard thiosulfate solution. Fe(II) was

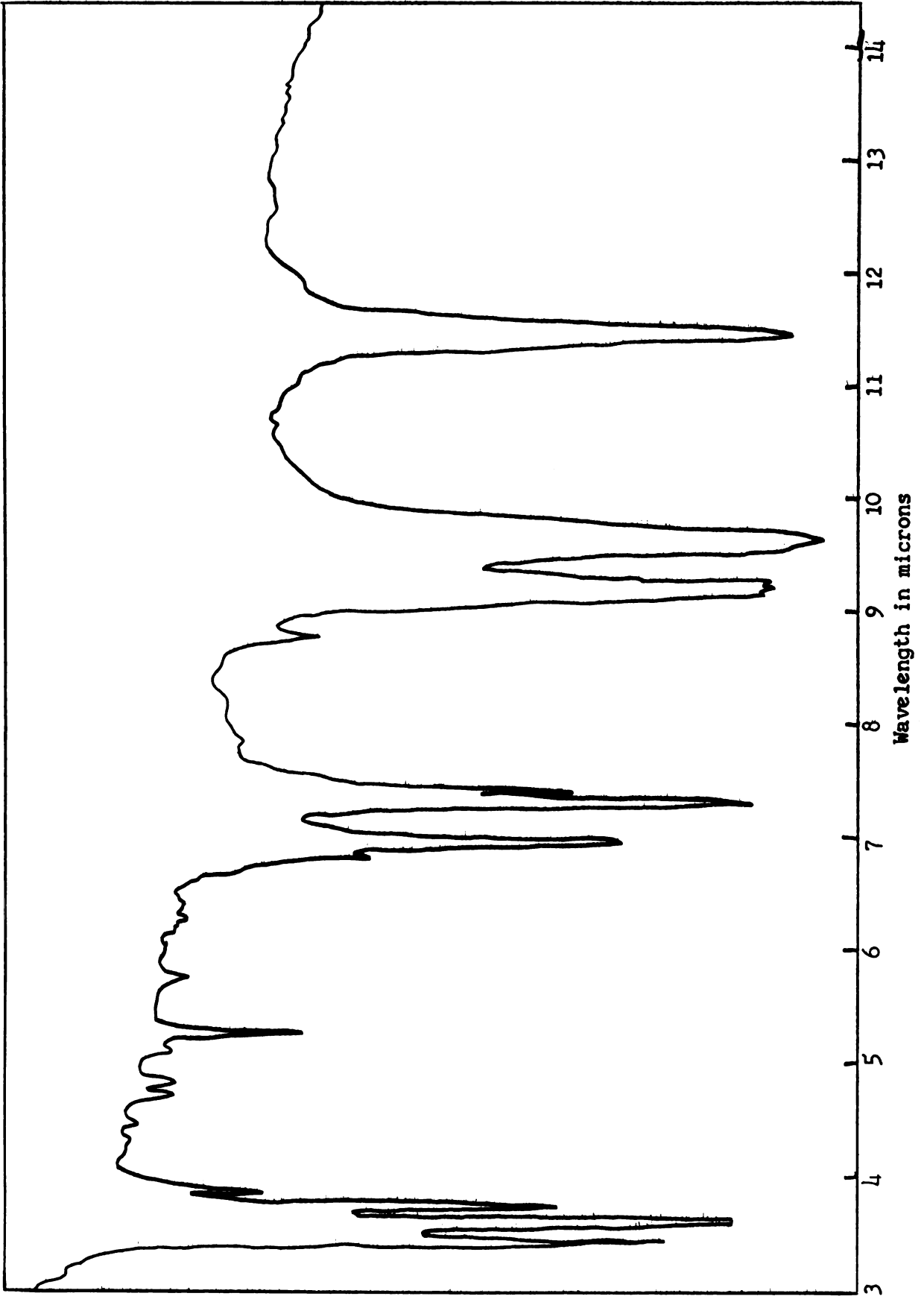


Figure 1. Infrared spectrum of TiOC_2H_5

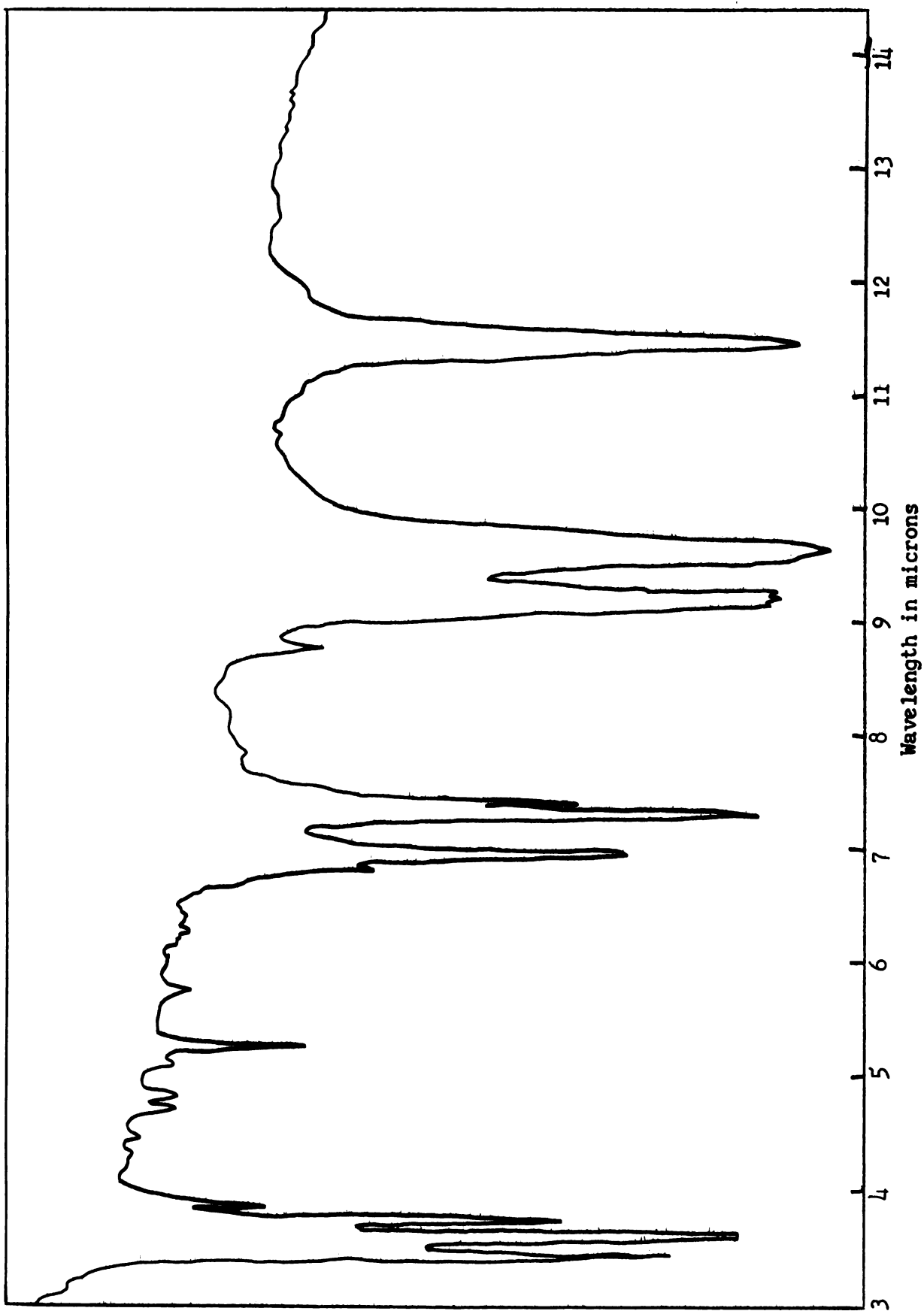


Figure 1. Infrared spectrum of TiOC_2H_5

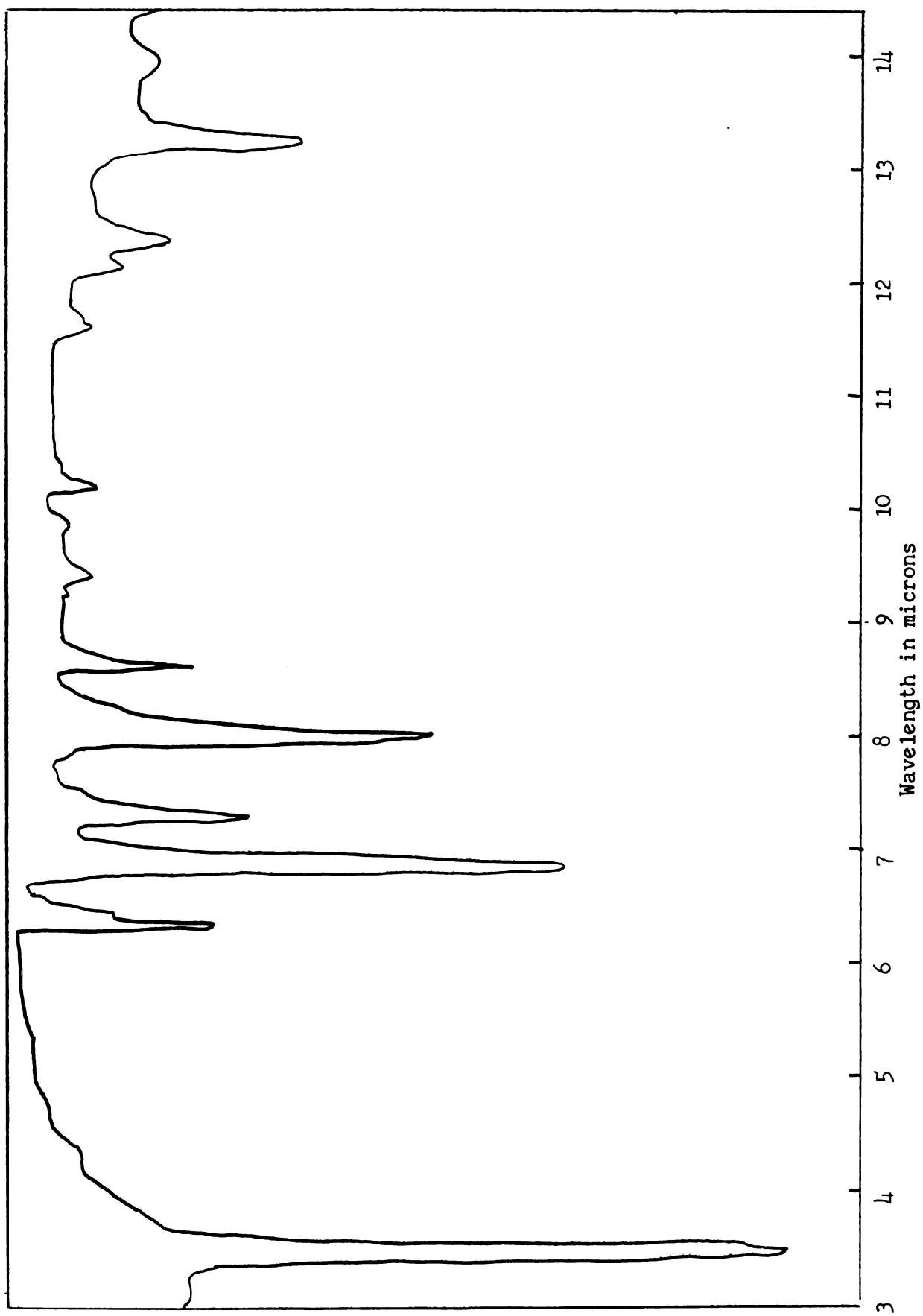


Figure 2. Infrared spectrum of $\text{Tl}(\text{OC}_6\text{H}_5)$. (Nujol mull)

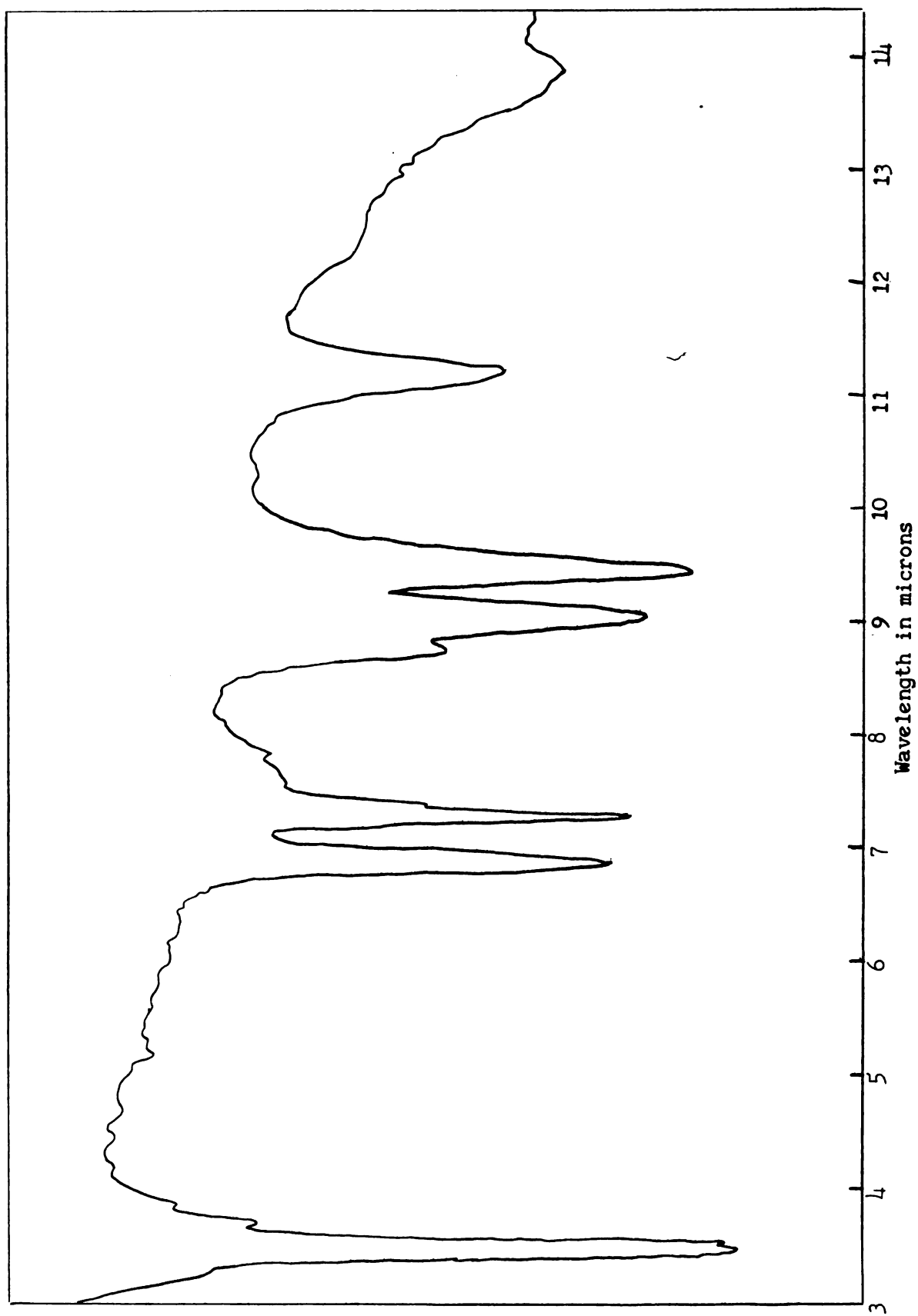


Figure 3. Infrared spectrum of $\text{Fe}(\text{OC}_2\text{H}_5)_3$. (Nujol mull)

determined by titration with standard $\text{Ce}(\text{SO}_4)_2$ after the samples were hydrolyzed in dilute H_2SO_4 .

Copper Analysis. $\text{Cu}(\text{II})$ samples were hydrolyzed in dilute HCl , and after the addition of potassium iodide, the liberated iodine was titrated with standard thiosulfate solution (39).

Uranium and Aluminum Analysis. Uranium was separated from aluminum by formation of the peroxide (40), and was then analyzed by ignition to U_3O_8 . Aluminum was determined by precipitation of the hydrous oxide and subsequent ignition to the oxide.

Thallium Analysis. Thallium (I) was separated from iron in all samples by precipitation of the thallium (I) thiourea complex (41). The complex was then dissolved in hot water and thalious chromate was precipitated by addition of potassium chromate. This was dried at 110° and weighed as Tl_2CrO_4 (42).

Phenoxide Analysis. After hydrolysis of $\text{Fe}(\text{OC}_6\text{H}_5)_3$ in basic solution, phenoxide was determined by the bromination of phenol, reaction of the excess bromine with KI , and titration of the liberated iodine with thiosulfate (43).

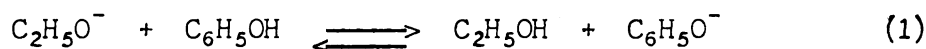
Carbon and Hydrogen Analysis. These were performed by Spang Micro-analytical Laboratory, Ann Arbor, Michigan.

Preparation of Compounds

In all procedures involving the use or synthesis of moisture sensitive materials, the utmost care was used to avoid contact with moisture.

Flasks were always flushed with nitrogen before use, and all critical operations such as filtration, transfer of solutions, etc., were always done in a nitrogen atmosphere dry-box.

Iron (III) Phenoxide. To 200 ml. of ethanol, 2.91 grams (0.127 moles) of sodium was added. After the sodium metal had completely reacted, 11.29 grams (0.127 moles) of phenol was added, and the flask was heated gently until the phenol dissolved. The following equilibrium then exists in solution:



6.85 grams (0.0422 moles) of ferric chloride was added and an exothermic reaction ensued. The solution became blood red and a cream colored precipitate formed. After refluxing for two hours, the ethanol was distilled under reduced pressure thus forcing the equilibrium (1) to the right. The red solid residue was extracted with three 50 ml. portions of benzene. Partial evaporation of the benzene solution plus addition of 100 ml. of petroleum ether caused the precipitation of a black solid which was filtered and washed with petroleum ether. The product (8.52 grams) was obtained in a 60.2% yield although more could have been isolated by continued extraction. Upon grinding the black solid became dark red. The infrared spectrum is presented in Figure 4. However, no visible spectrum could be obtained because a charge transfer band completely obscured any details of this region.

Analysis: Calc'd for $\text{Fe}(\text{OC}_6\text{H}_5)_3$: Fe, 16.66; OC_6H_5 , 83.34.

Found: Fe, 16.37; OC_6H_5 , 83.60.

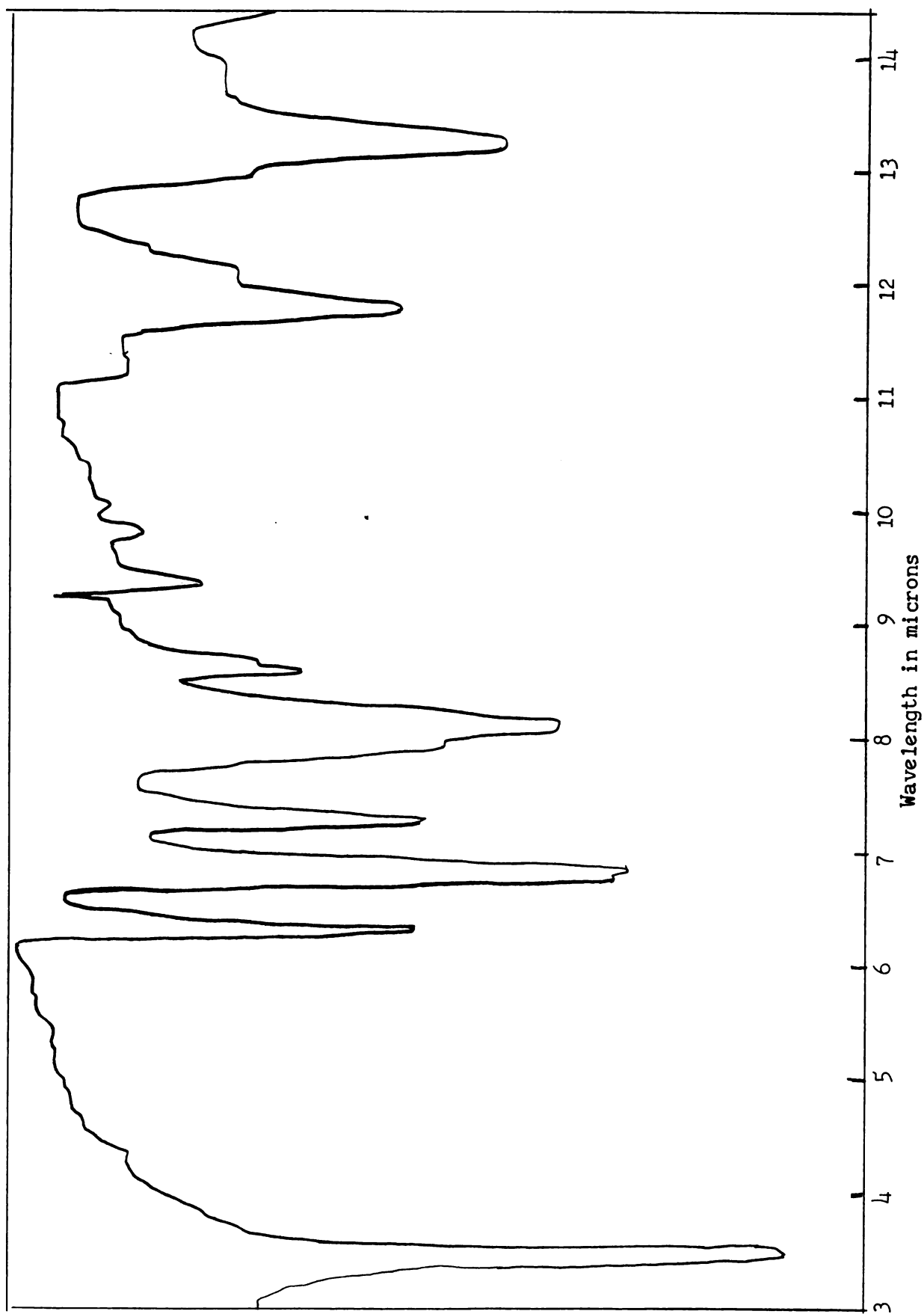


Figure 4. Infrared spectrum of $\text{Fe}(\text{OC}_6\text{H}_5)_3 \cdot$ (Nujol mull)

Copper (II) Methoxide. Lithium methoxide was prepared in situ by adding 0.542 grams (0.078 moles) of lithium to 100 ml. of methanol. Fifty milliliters of a methanolic 0.78 M. CuCl_2 solution was slowly added to this in an erlenmeyer flask, and a light silky green precipitate formed. Agitation of this mixture by rapid shaking, changed the color of the precipitate from green to deep blue. The coarse blue solid was then filtered on a sintered glass frit, washed with methanol and then dried in vacuo, 3.00 grams was recovered in an 89.5 % yield. The infrared and visible spectra are presented in Figures 5 and 6 respectively.

Analysis: Calc'd for $\text{Cu}(\text{OCH}_3)_2$: Cu, 50.59; C, 19.12; H, 4.82.

Found: Cu, 50.57; C, 18.99; H, 4.67.

Copper (II) Chloridemethoxide. Investigation of the previous reaction revealed that the green precipitate was a different species, $\text{Cu}(\text{OCH}_3)\text{Cl}$. The green solid can be prepared in three different ways.

From the previously mentioned reaction, when the supernatant liquid was carefully decanted from the green precipitate without any agitation, the green solid was isolated.

Addition of CuCl_2 to a suspension of $\text{Cu}(\text{OCH}_3)_2$ in methanol, caused the color of the solid to turn from blue to green. The reaction was complete when excess CuCl_2 colored the previously clear methanol.

In contrast to the previous two methods, when a solution of LiOCH_3 in methanol was added to a solution of CuCl_2 in methanol, green $\text{Cu}(\text{OCH}_3)\text{Cl}$ formed as long as CuCl_2 was present in excess.

In all three methods the solid was filtered on a sintered glass frit, washed with methanol, and dried in vacuo. The infrared and visible spectra are presented in Figures 7 and 6 respectively.

Analysis: Calc'd for $\text{Cu}(\text{OCH}_3)\text{Cl}$: Cu, 48.88; C, 9.24; H, 2.32.

Found: Cu, 49.16; C, 9.31; H, 2.30.

Copper (II) Ethoxide. This was made exactly as the corresponding methoxide using lithium ethoxide and ethanol. The reaction is quantitative and the product which precipitates is blue-green. The carbon and hydrogen analysis of this compound, however, is reported as being quite low although the metal analysis is very satisfactory. It is suspected that hydrolysis occurred in the process of analysis. In the synthesis and handling of this compound, very strict measures were taken to exclude moisture. The infrared spectrum of this compound shows no bands due to the hydroxyl group or water as is usually found when hydrolysis has occurred. The infrared and visible absorption spectra are presented in Figures 8 and 9 respectively.

Analysis: Calc'd for $\text{Cu}(\text{OC}_2\text{H}_5)_2$: Cu, 41.34; C, 31.26; H, 6.59.

Found: Cu, 41.04; C, 27.55; H, 6.01.

Copper (II) Chloride Ethoxide. This was synthesized as the analagous copper (II) chloride methoxide, using lithium ethoxide and ethanol. The green product was quantitatively precipitated and recovered. The infrared and visible absorption spectra are presented in Figures 10 and 9 respectively.

Analysis: Calc'd for $\text{Cu}(\text{OC}_2\text{H}_5)\text{Cl}$: Cu, 44.09; C, 16.67; H, 3.50.

Found: Cu, 43.38; C, 16.58; H, 3.51.

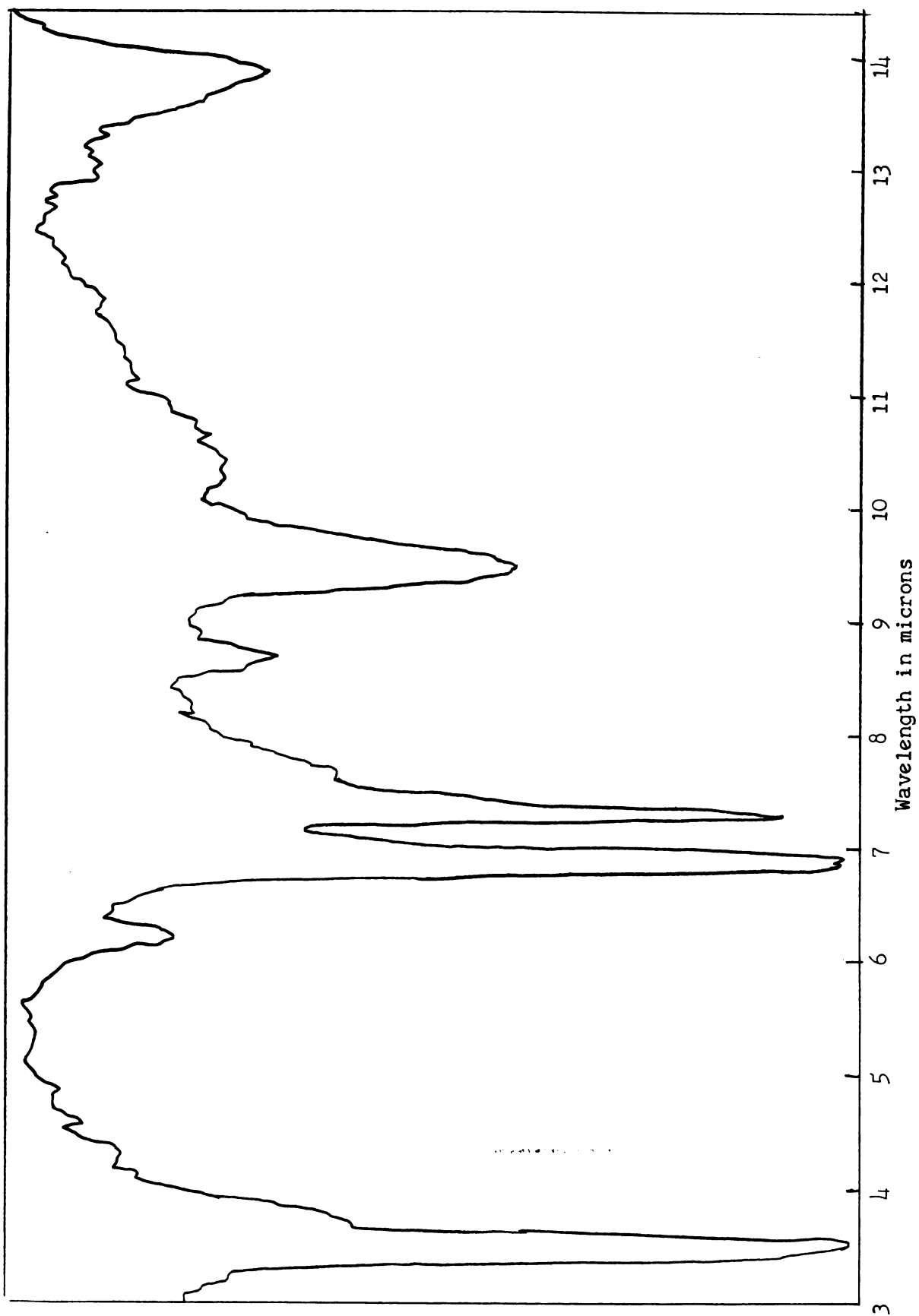


Figure 5. Infrared spectrum of $\text{Cu}(\text{OCH}_3)_2 \cdot (\text{Nujol mull})$

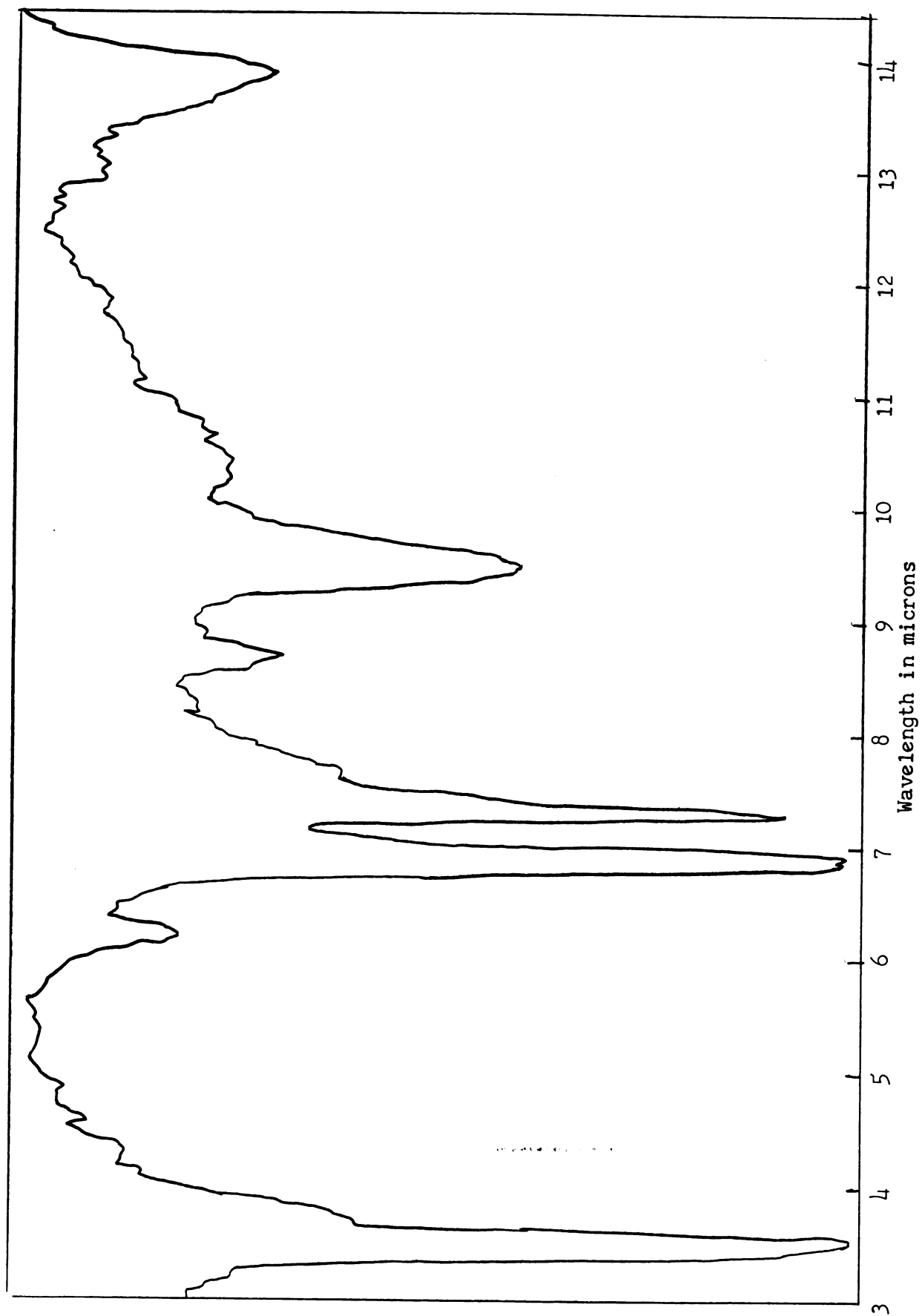


Figure 5. Infrared spectrum of $\text{Cu}(\text{OCH}_3)_2 \cdot (\text{Nujol mull})$

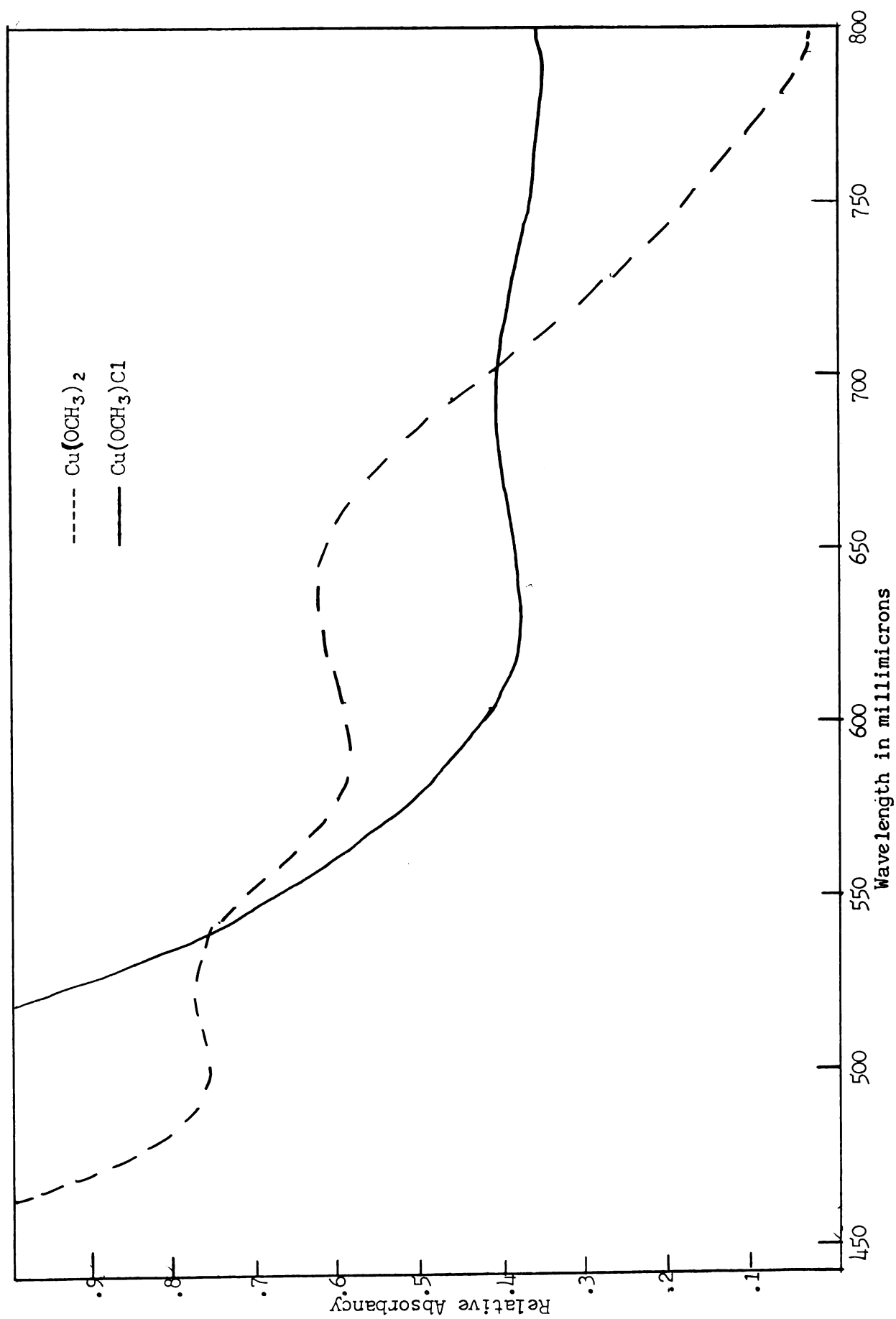


Figure 6. Visible absorption spectra of $\text{Cu}(\text{OCH}_3)_2$ and $\text{Cu}(\text{OCH}_3)\text{Cl}$. (Nujol mull)

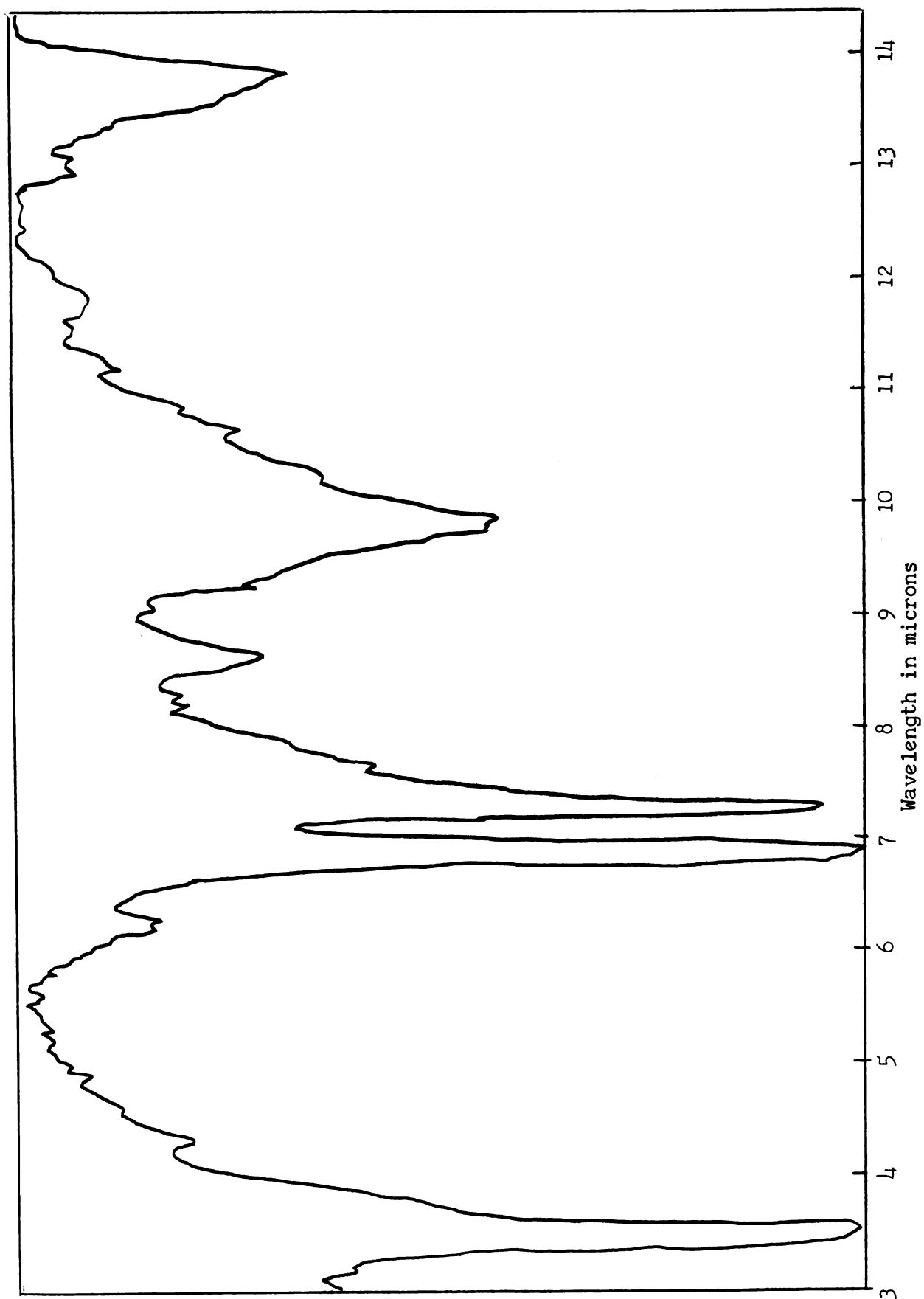


Figure 7. Infrared spectrum of $\text{Cu}(\text{OCH}_3)\text{Cl}$. (Nujol mull)

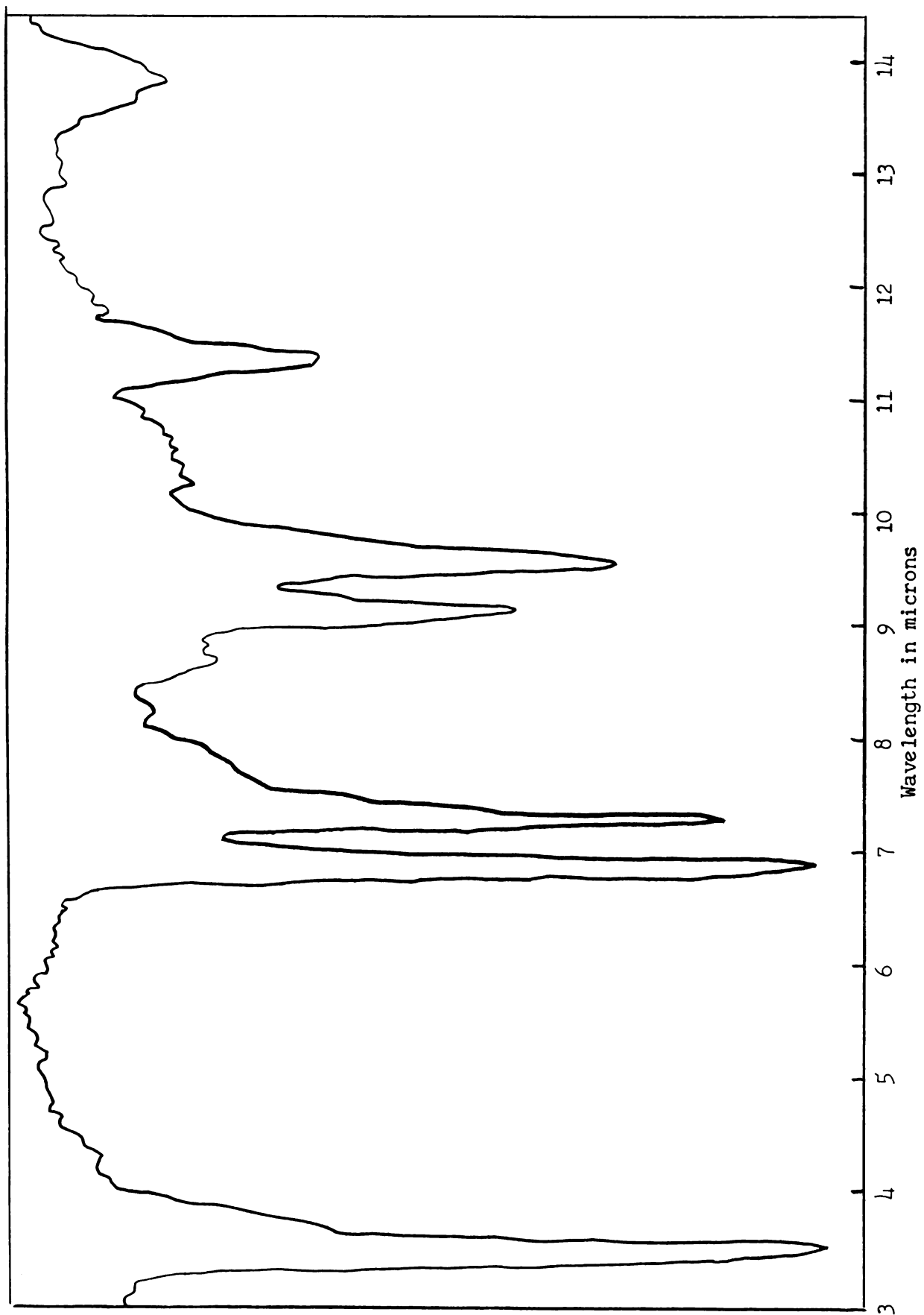


Figure 8. Infrared spectrum of $\text{Cu}(\text{OC}_2\text{H}_5)_2 \cdot (\text{Nujol mull})$.

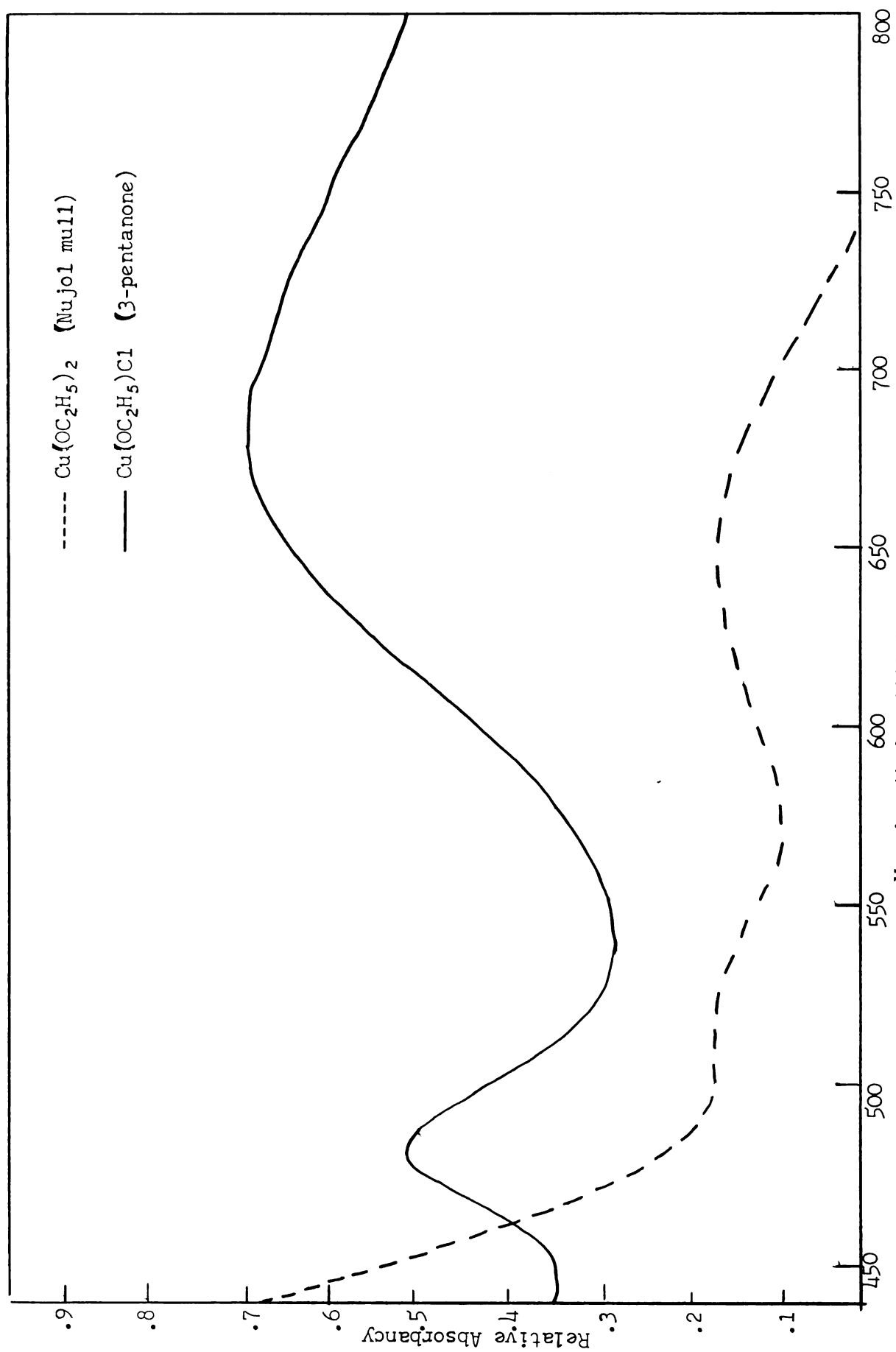


Figure 9. Visible absorption spectra of $\text{Cu}(\text{OC}_2\text{H}_5)_2$ and $\text{Cu}(\text{OC}_2\text{H}_5)_2\text{Cl}$.

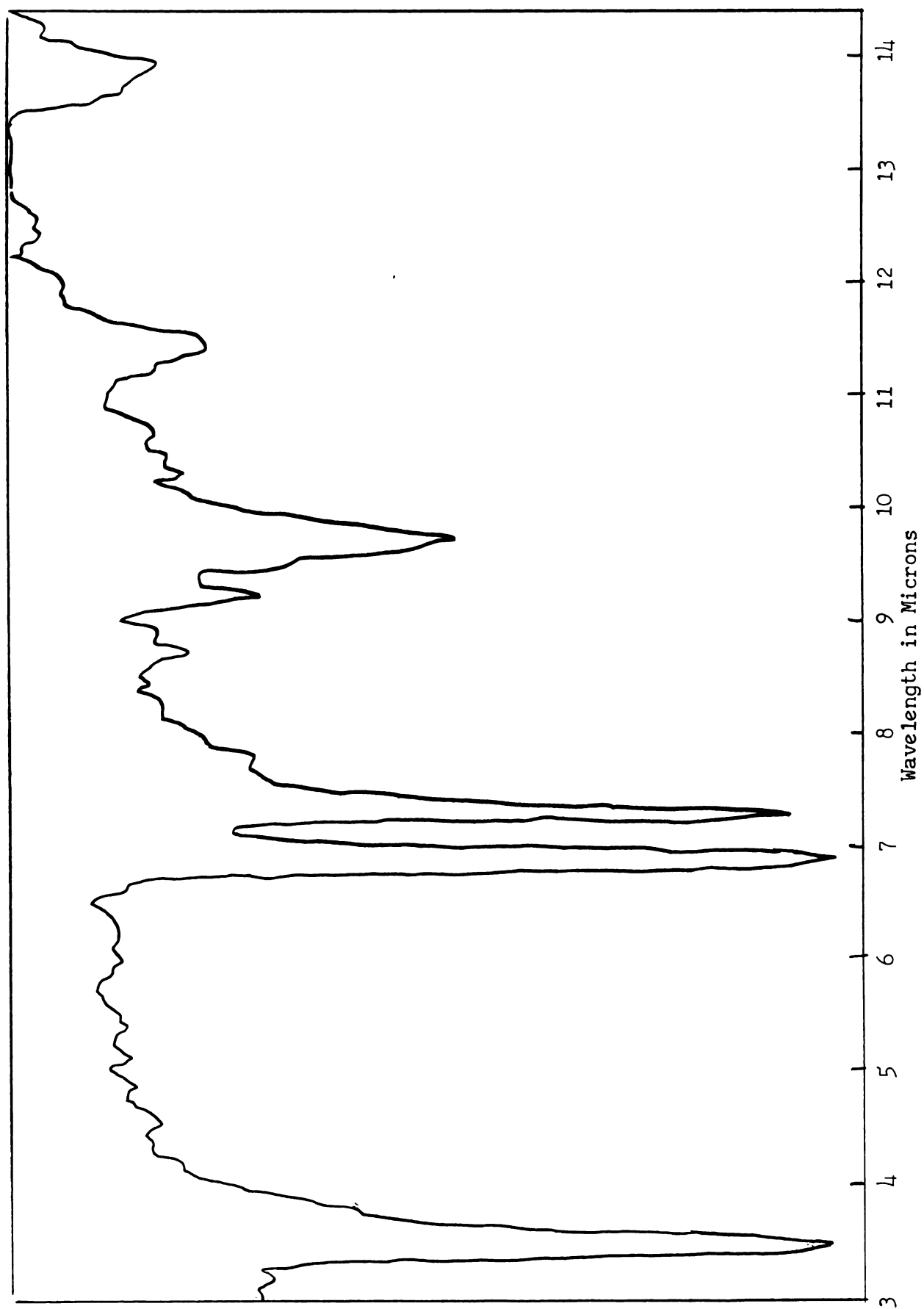


Figure 10. Infrared spectrum of $\text{Cu}(\text{OC}_2\text{H}_5)\text{Cl}$. (Nujol mull)

Mixed Metal Alkoxides

Uranium (IV) tetrakis (tetraisopropoxoaluminate): This compound was made according to the method of Albers (31). Sodium isopropoxide was added to 100 ml. of a 1.6 M aluminum isopropoxide solution until all the $\text{NaAl}(\text{OC}_3\text{H}_7^i)_4$ had precipitated. To this was added, 169 ml of a 0.180 M solution of UCl_4 in isopropanol. From this dirty green mixture, the viscous green double alkoxide could be isolated by vacuum distillation. The liquid is subject to rapid hydrolysis and oxidation and showed noticeable decomposition within a week, even when stored under nitrogen in a dry-box.

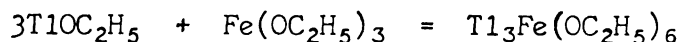
The infrared spectrum is presented in Figure 11. The visible spectrum showed only a broad charge transfer band. No E.P.R. signal could be detected for the sample when measured pure or as a solution in benzene.

Analysis: Calc'd for $\text{UAl}_4(\text{OC}_3\text{H}_7^i)_{16}$: U, 18.43; Al, 8.36.

Found: U, 18.82; Al, 8.89.

Attempted Preparation of a Thallium (I), Iron (III) Double Alkoxide.

Two procedures were tried without success for isolating a double alkoxide. The reactants were added according to the following stoichiometry



To a solution of 0.0033 moles of $\text{Fe}(\text{OC}_2\text{H}_5)_3$ in CCl_4 , 0.01 moles of TlOC_2H_5 were added; 40 ml of absolute ethanol was added, and a very small amount of light orange precipitate formed. This was filtered and analysis showed less than 5% iron. The infrared spectrum showed no alkoxide absorption bands, and the substance did not burn in a flame.

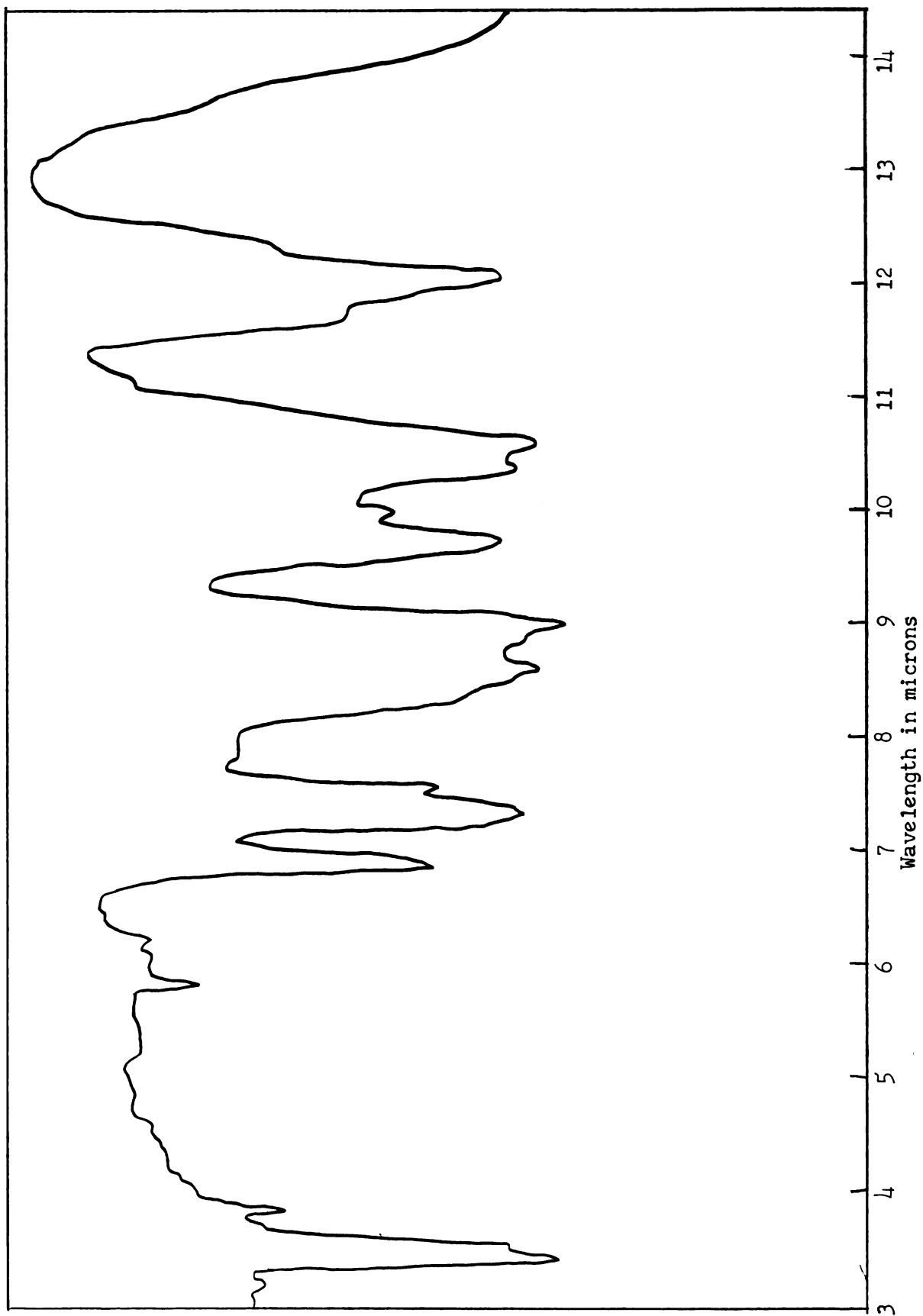


Figure 11. Infrared spectrum of $\text{UA1}_4(\text{OC}_3\text{H}_7^i)_{16}$.

In the second method, benzene was used as the solvent. To 25 ml. of a 0.0133 M $\text{Fe}(\text{OC}_2\text{H}_5)_3$ benzene solution, 0.01 mole of TiOC_2H_5 was then added. No precipitate was noticed. Removal of the solvent under reduced pressure yielded a tan solid. This was washed with ethanol and benzene until the filtrate was colorless. The resultant tan solid showed no alkoxide absorption in the infrared and also did not burn in a flame. It is assumed that decomposition took place, and the solid residue is mainly thalious ferrate (III).

Analysis: Calc'd for TiFeO_2 : Ti, 69.93; Fe, 19.11.

Found: Ti, 67.06; Fe, 19.02.

Attempted Preparation of a Thallium (I), Iron (III) Double Phenoxide.

Forty milliliters of a saturated benzene solution of thallium (I) phenoxide was added to 40 ml of a saturated benzene solution of iron (III) phenoxide. The solution was refluxed for five hours but no precipitate formed. Upon slow evaporation of the solvent, the white thallium (I) phenoxide began to crystallize from the solution. Hence it was concluded that no reaction occurred.

Attempted Preparation of a Cobalt (II), Titanium (IV) Double Alkoxide.

A different type of reaction was attempted as compared to that used for iron and thallium. Since cobalt (II) alkoxides are unknown, it was thought that cobalt (II) chloride might react with an equimolar amount of sodium isopropoxide and titanium isopropoxide ($\text{NaTi}(\text{OC}_3\text{H}_7^i)_5$) in isopropanol. Accordingly 0.0532 moles of both $\text{NaOC}_3\text{H}_7^i$ and $\text{Ti}(\text{OC}_3\text{H}_7^i)_4$ were added to 200 ml of isopropanol. To this 0.0262 moles of CoCl_2 was added, and the resultant blue solution was refluxed for eight hours.

After the removal of the solvent under reduced pressure, the residue was extracted with benzene and filtered. A blue solid was then precipitated by subsequent addition of petroleum ether. This solid contained chlorine but not titanium. Bartley (30) by the similar reaction of CoCl_2 with $\text{NaZr}_2(\text{OC}_3\text{H}_7^i)_9$ isolated a similar blue solid which contained no zirconium and was found to be $\text{Na}_2[\text{Co}(\text{OC}_3\text{H}_7^i)_2\text{Cl}_2]$. The infrared and visible spectra are presented in Figures 12 and 13.

Attempted Preparation of an Iron (II), Titanium (IV) Double Alkoxide.

The reaction was done similarly to that with CoCl_2 , using the same stoichiometry. However, upon addition of the iron (II) chloride, a large quantity of brown precipitate formed. This was of a very muddy texture and could be filtered only with the greatest of difficulty. It was filtered and dried under vacuum to yield a light brown powder. This solid did not burn, did not absorb in the infrared, was contaminated with sodium chloride, and was not soluble in common organic solvents.

Analogously when FeCl_2 was added to solutions of sodium isopropoxide in isopropanol, sodium ethoxide or lithium ethoxide in ethanol, and sodium methoxide or lithium methoxide in methanol, the same muddy type of precipitate resulted. The precipitates from the reactions involving the lithium alkoxides were, however, uncontaminated with lithium chloride, and hence the precipitate should have been a pure alkoxide. Analysis for Fe(II) showed, however, less than 10% in both cases. It seems then most probable that oxidation had occurred and that regardless of whether $\text{NaTi}(\text{OC}_3\text{H}_7^i)_5$, NaOC_2H_5 , or LiOC_2H_5 are used, no definite product can be isolated.

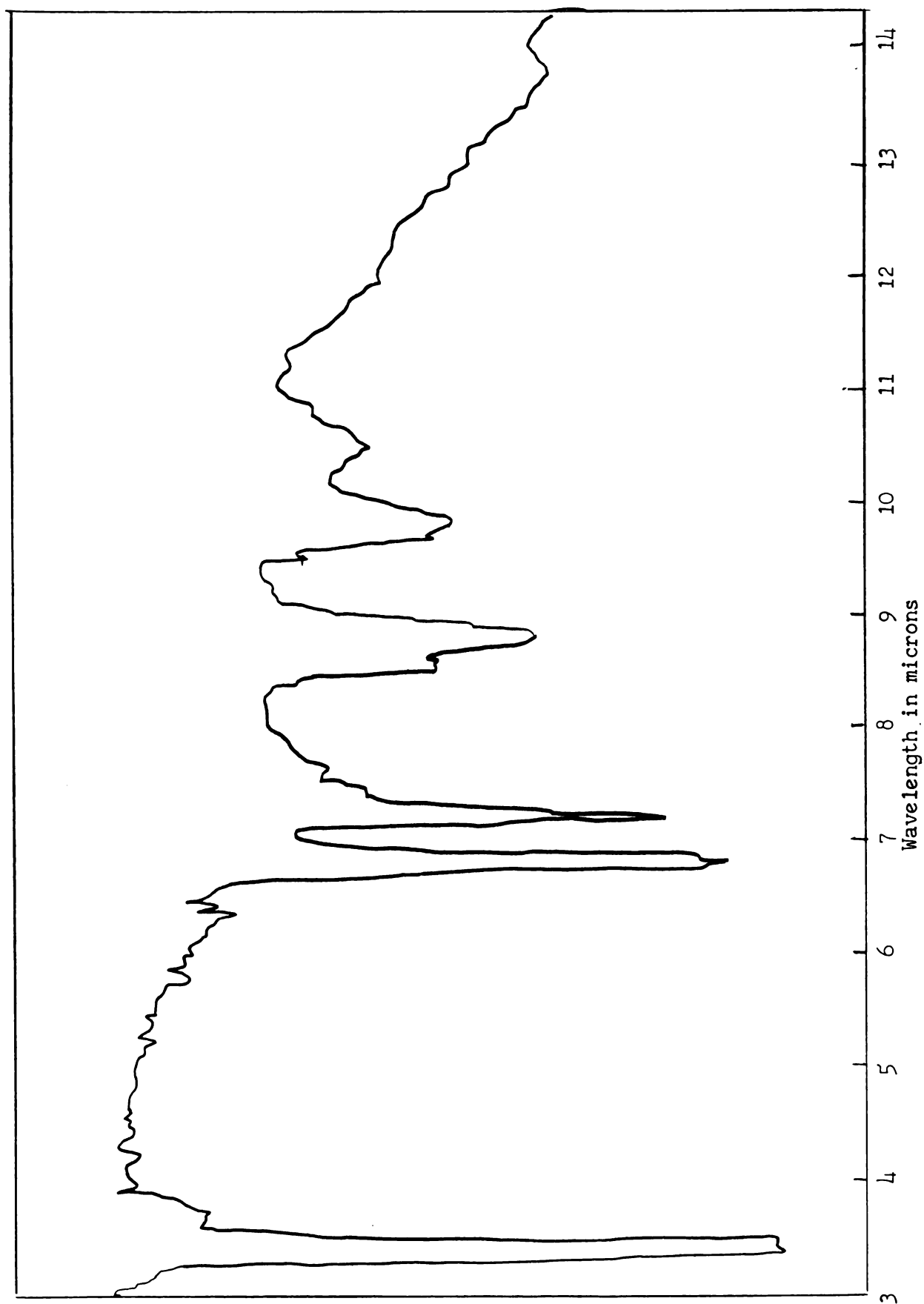


Figure 12. Infrared spectra of $\text{Na}_2[\text{Co}(\text{OC}_3\text{H}_7^i)_2\text{Cl}_2]$. (Nujol mull)

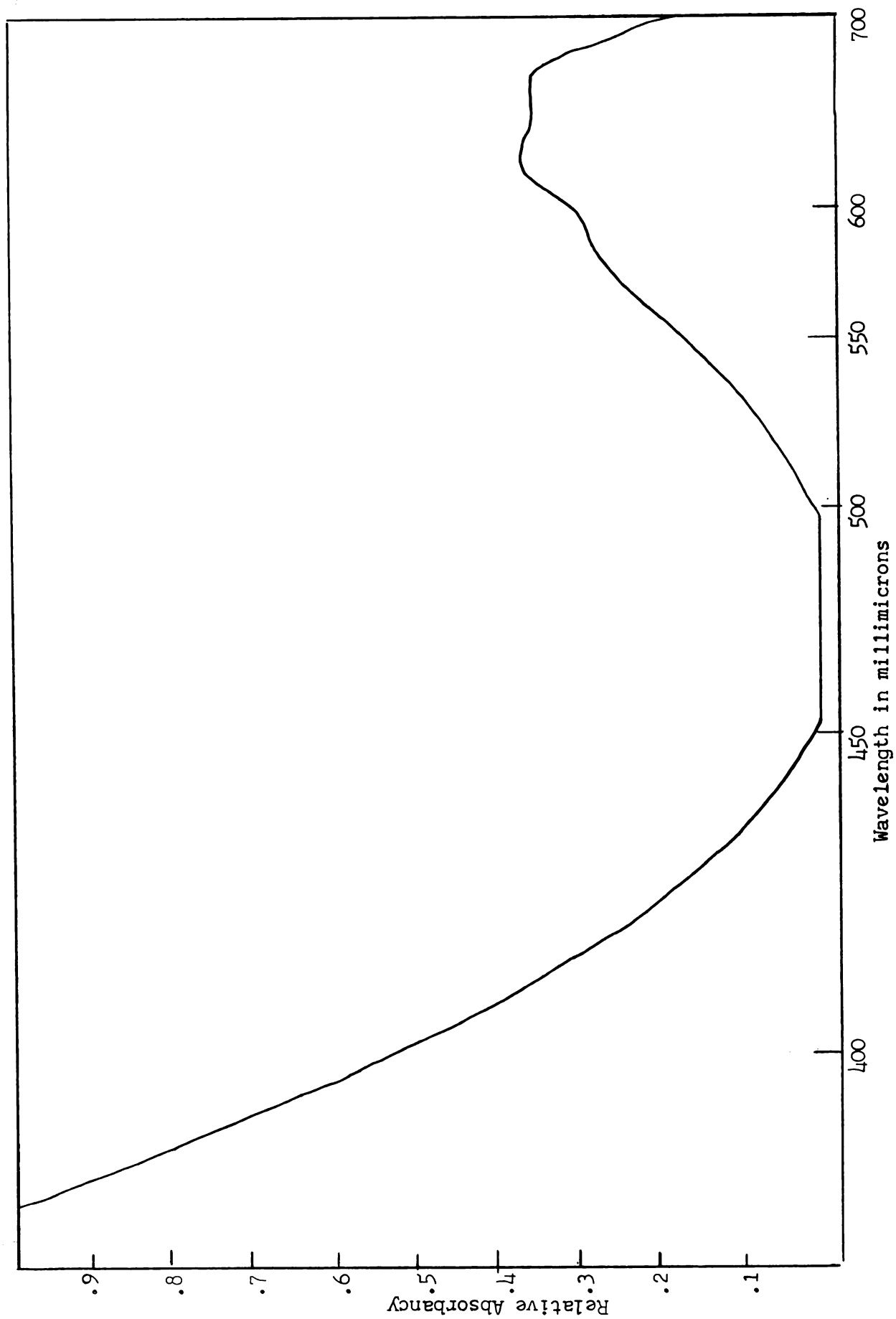


Figure 13. Visible absorption spectrum of $\text{Na}_2[\text{Co}(\text{OC}_3\text{H}_7^i)_2\text{Cl}_2]$. (Isopropanol)

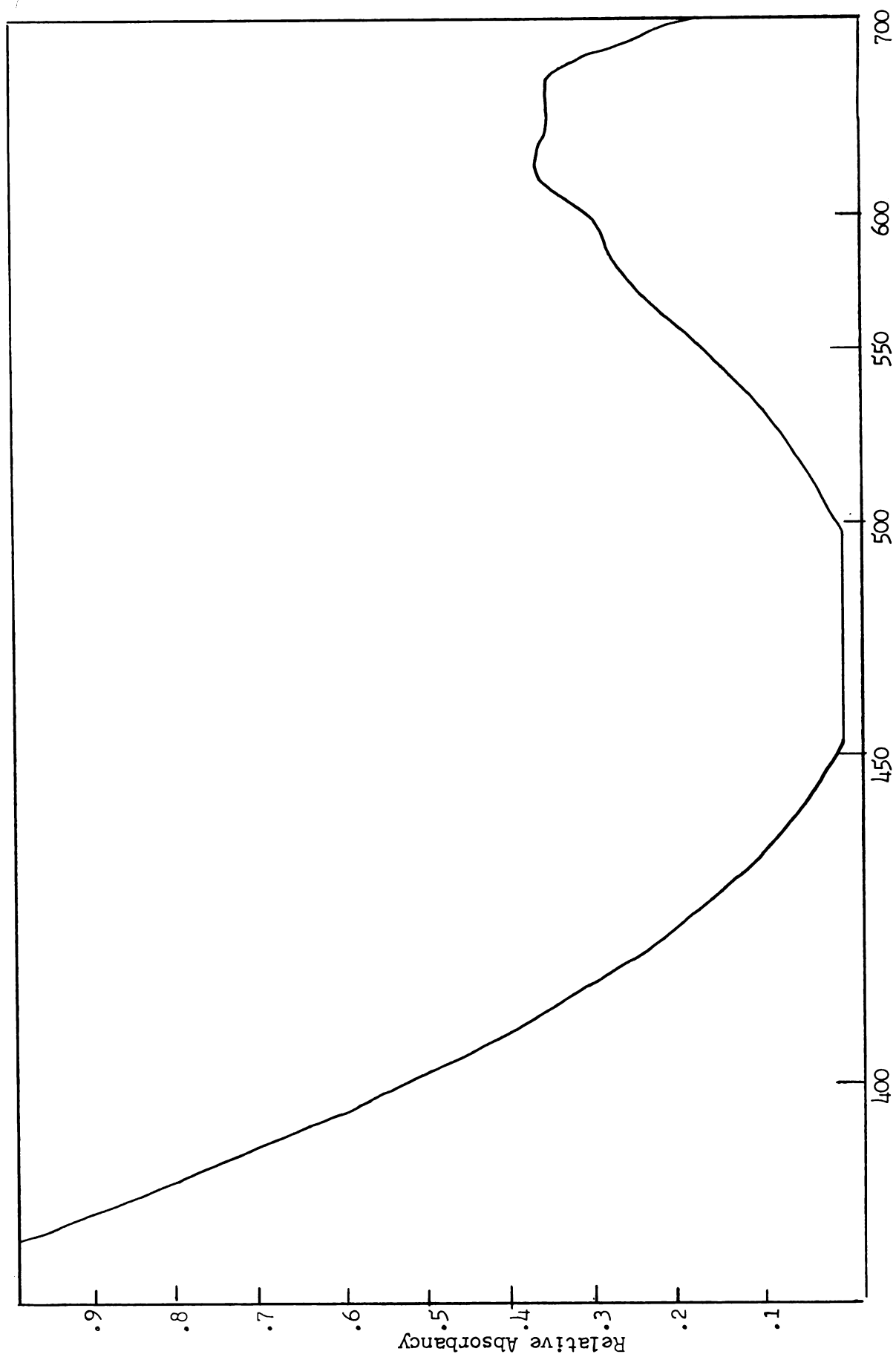


Figure 13. Visible absorption spectrum of $\text{Na}_2[\text{Co}(\text{OC}_3\text{H}_7^i)_2\text{Cl}_2]$. (Isopropanol)

Spectroscopic Measurements

All infrared spectra were obtained with the Perkin-Elmer Model 21 Spectrophotometer. All solid samples were milled in Nujol.

The visible spectra have been obtained with a Beckman Model DB Spectrophotometer. Most of the solids were milled in Nujol since no solvent was available. All mulls and solutions necessary for the visible and infrared spectra of moisture sensitive compounds were prepared in a dry-box.

Magnetic Susceptibility Measurements

Magnetic susceptibilities were determined by the Gouy method, employing a semi-micro balance and the electromagnet described by Vander Vennan (44). The susceptibility was calculated by use of the following equation

$$X \times 10^6 = \frac{\beta F' + \alpha}{W}$$

where X is the gram susceptibility; W is the weight in grams of the sample; β is the tube constant; F' is the corrected force in mg. and is equal to the force, F, experienced by the sample plus the force, δ , experienced by the glass tube; α is a constant allowing for the susceptibility of the displaced air.

The mole susceptibility, X_m , can be calculated by multiplying the gram susceptibility, X, of the sample by the molecular weight. X_m' , the corrected mole susceptibility, is obtained from X_m by adding to it the appropriate Pascal constants--the corrections for the diamagnetic ligands (45).

The magnetic moment, μ , is then calculated from the following equation:

$$\mu = 2.84[X_m'(T + \Theta)]^{1/2}$$

The Curie-Weiss temperature, Θ , was not calculated for any of the compounds and was assumed to be small.

The tube which has a standard tapered glass joint to prevent hydrolysis of samples was calibrated with both $\text{Hg}[\text{Co}(\text{SCN})_4]$ and water (46). $\text{Hg}[\text{Co}(\text{SCN})_4]$ was used for the calibration at low field strength and was suitable for determining the susceptibility of samples having two or more unpaired electrons. The calibrant has a gram susceptibility of 16.44×10^{-6} at 20° . To calculate the gram susceptibility of the calibrant at any given temperature, the following equation is used

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

M is the molecular weight, 481.9, C , 177×10^{-6} , is the diamagnetic correction for $\text{Hg}[\text{Co}(\text{SCN})_4]$, Θ equals 10° , and μ equals 4.44 Bohr Magnetons (47). Substitution yields the following:

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

The tube was calibrated at 23° and 28° , where the gram susceptibility was respectively 16.27×10^{-6} and 16.00×10^{-6} .

For water which is useful as a calibrant when the samples are diamagnetic or have one unpaired electron, the gram susceptibility is -0.720×10^{-6} at 20° and $dX/dT = 0.0012/\text{degree}$ at 20° (46).

The results for the compounds measured are presented in Table I.

Table I. Magnetic susceptibilities and moments

Compound	Temp. °K	$\chi_m' \times 10^6$	μ (B.M.)
$\text{Cu}(\text{OCH}_3)_2$	297	528	1.12
	296	480	1.07
$\text{Cu}(\text{OCH}_3)\text{Cl}$	297	1,160	1.67
	298	1,180	1.68
$\text{Cu}(\text{OC}_2\text{H}_5)_2$	296	579	1.18
	296	636	1.23
$\text{Cu}(\text{OC}_2\text{H}_5)\text{Cl}$	299	828	1.41
	296	810	1.39
$\text{Fe}(\text{OC}_6\text{H}_5)_3$	301	34,400	9.14
	301	36,000	9.28
$\text{Fe}(\text{OC}_2\text{H}_5)_3$	301	9,890	4.91
	301	9,720	4.85
$\text{Na}_2[\text{Co}(\text{OC}_3\text{H}_7^i)_2\text{Cl}_2]$	298	8,860	4.60
$\text{UAl}_4(\text{OC}_3\text{H}_7^i)_{16}$	300	4,230	3.21

RESULTS AND DISCUSSION

Copper (II) Alkoxides and Chloride Alkoxides

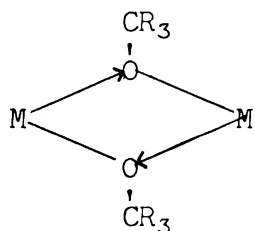
The alkoxides synthesized, $\text{Cu}(\text{OCH}_3)_2$ and $\text{Cu}(\text{OC}_2\text{H}_5)_2$ are seemingly quite different from the typical transition metal alkoxides in that they are not volatile or soluble in inert solvents. However, they do resemble a second type of alkoxide--that typified by $\text{V}(\text{OCH}_3)_3$, $\text{U}(\text{OCH}_3)_4$, or $\text{La}(\text{OCH}_3)_3$. The compounds are generally insoluble and have the metal ions in a low oxidation state and with small ionic radii. These alkoxides are probably covalent polymers as contrasted to the usual small telemeric metal alkoxides.

The chloride alkoxides, too, have different properties from the known chloride alkoxides, e.g., titanium (IV) and zirconium (IV) (48). The chloride alkoxides of the aforementioned elements are considered to be covalent and similar to the parent alkoxides, whereas the chloride alkoxides of copper (II) resemble the copper (II) alkoxides in chemical properties.

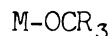
Before postulating possible structures for these new compound, it is first necessary to consider the spectra, both visible and infrared, magnetic properties, and chemical properties of the compounds.

The infrared spectra of methoxides or ethoxides are relatively simple in the region where the C-O stretching vibration band appears. For the methoxides a single, strong wide band occurs between 1020-1100 cm^{-1} , and for the ethoxide this band appears at 1025-1070 cm^{-1} . Barraclough (20) in a study of the infrared spectrum of metal alkoxides, postulated that two C-O stretching vibration bands are possible because

of the difference between terminal and bridging alkoxide groups in covalent metal alkoxides.



bridging



terminal

Such differences between bridging and terminal groups have been noted in compounds having CO, CN^- , SCN^- , and NO as ligands. Two or more absorption bands are attributable to the stretching vibrations of these groups (49). However, alkoxide ligands do not show two such distinct bands in the region of the C-O stretching vibration. Because the C-O band is very broad and the region of absorption is at best double the half-width of the C-O band, one would expect superimposition of terminal and bridging group absorptions, or possibly the presence of a shoulder when both types of alkoxide groups are present simultaneously in a molecule. As expected, then, only one band is found for the ethoxide or methoxide ligand not only in the compounds synthesized in this research, but also in the spectra reported in the literature (4,14,20,50,51). It is thus the position of the single band (and in few cases an accompanying shoulder) which could be indicative of the type of alkoxide linkage present.

Inspection of the position of the C-O stretching band reveals that there are three rather distinct regions of absorption. The alkoxides, listed in Tables II and III with the frequencies of the bands, are classified according to the region in which the C-O band appears. Compounds

Table II. C-O absorption bands of methoxides.

Compound	Region of Absorption (cm^{-1})		
	I	II	III
$[(\text{CH}_3)_4\text{N}]_2[\text{Nb}(\text{OCH}_3)\text{Cl}_5]$ (50)	1130	---	---
$(\text{C}_5\text{H}_6\text{N})_2[\text{Nb}(\text{OCH}_3)\text{Cl}_5]$ (50)	1095	---	---
$(\text{C}_9\text{H}_8\text{N})_2[\text{Nb}(\text{OCH}_3)\text{Cl}_5]$ (50)	1110	---	---
$\text{Cu}(\text{OCH}_3)_2$	---	1056	---
$\text{Cu}(\text{OCH}_3)\text{Cl}$	---	---	1014
TiOCH_3 (4)	---	---	1030

Table III. C-O absorption bands of ethoxides.

Compound	Region of Absorption (cm^{-1})		
	I	II	III
$[(\text{CH}_3)_2\text{NH}_2]_2[\text{Nb}(\text{OC}_2\text{H}_5)\text{Cl}_5]$ (50)	1070	---	---
$(\text{C}_5\text{H}_6\text{N})_2[\text{Nb}(\text{OC}_2\text{H}_5)\text{Cl}_5]$ (50)	1070	---	---
$(\text{C}_9\text{H}_8\text{N})_2[\text{Nb}(\text{OC}_2\text{H}_5)\text{Cl}_5]$ (50)	1070	---	---
$\text{Ti}(\text{OC}_2\text{H}_5)_4$ (20)	1064	---	1042(sh)*
$\text{Ta}(\text{OC}_2\text{H}_5)_5$ (20)	1072	---	1030(sh)
$\text{Nb}(\text{OC}_2\text{H}_5)_5$ (20)	1063	---	1029(sh)
$\text{Nb}(\text{OC}_2\text{H}_5)_4$ (14)	---	1060	---
$\text{Al}(\text{OC}_2\text{H}_5)_3$ (51)	---	1059	---
$\text{Fe}(\text{OC}_2\text{H}_5)_3$	---	1060	---
$\text{Cu}(\text{OC}_2\text{H}_5)_2$	---	1049	---
$\text{Cu}(\text{OC}_2\text{H}_5)\text{Cl}$	---	---	1027
TiOC_2H_5	---	---	1030

*(sh) = shoulder.

absorbing in region (I) are believed to have terminal alkoxide groups only. Absorptions in region (II) are believed to be due to both terminal and bridging alkoxide groups, while absorption in region (III) is indicative of bridging alkoxides only. Thus by this classification, the copper (II) alkoxides would contain both terminal and bridging groups whereas the copper (II) chloride alkoxides would contain bridging groups only.

This distinction is very marked in the methoxides but less so in the ethoxides because of the smaller variation in the C-O stretching frequency. It is probable that in the higher analog alkoxides (propoxides, butoxides, etc.) the systematic variation in C-O stretching frequencies will not be noticeable because the strength of the intermolecular bridging bonds will be greatly reduced, hence causing negligible shifts in the C-O stretching frequency.

The visible absorption spectra of solutions and Nujol mulls of the copper (II) alkoxide and chloride alkoxide compounds have been measured, and the absorption maxima are listed in Table IV.

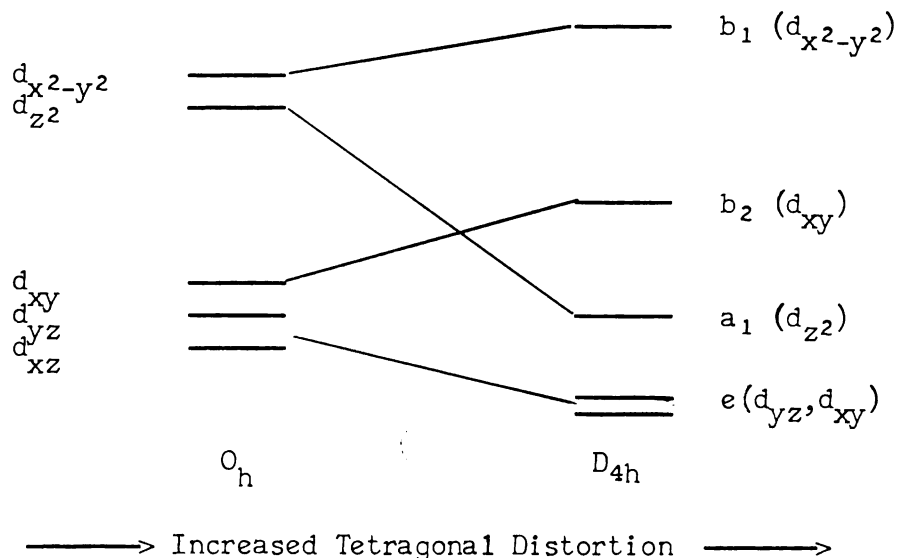
Table IV. Visible absorption maxima of copper (II) alkoxides and chloride alkoxides

Compound	Frequencies of Absorption (cm^{-1})		Medium
$\text{Cu}(\text{OC}_2\text{H}_5)_2$	19,400	15,500	Nujol
$\text{Cu}(\text{OC}_2\text{H}_5)\text{Cl}$	20,800	14,700	3-pentanone
$\text{Cu}(\text{OCH}_3)_2$	19,100	15,700	Nujol
$\text{Cu}(\text{OCH}_3)\text{Cl}$	---	14,500	Nujol

Of these spectra only that of $\text{Cu}(\text{OC}_2\text{H}_5)\text{Cl}$ is doubtful. Since the solvent is 3-pentanone, it is possible that some solvolysis has occurred and that the band at $20,800\text{ cm}^{-1}$ is due to coordinated solvent. (The spectrum of $\text{Cu}(\text{OC}_2\text{H}_5)\text{Cl}$ in Nujol contains no absorption bands.) This band is also present in the spectrum of CuCl_2 in 3-pentanone. In acetone, for example, the spectrum of $\text{Cu}(\text{OCH}_3)\text{Cl}$ corresponds exactly to that of CuCl_2 , hence a Nujol mull was used with this compound.

Copper (II) in an octahedral environment, should exhibit one symmetric band in the visible region corresponding to the ${}^2\text{E}_g \longrightarrow {}^2\text{T}_{2g}$ transition. Most spectra of Cu(II) complexes (for example aquo or ammine complexes), however, show one asymmetric band which can be resolved into two component bands (52). This asymmetry results from a tetragonal distortion as caused by the Jahn-Teller effect. In the limiting case of tetragonal distortion (a square planar configuration), three separate absorption bands are expected, and have been observed in copper (II) ethylacetylacetonate, for example (53).

The splitting of the d orbitals can be represented with respect to the amount of tetragonal distortion.



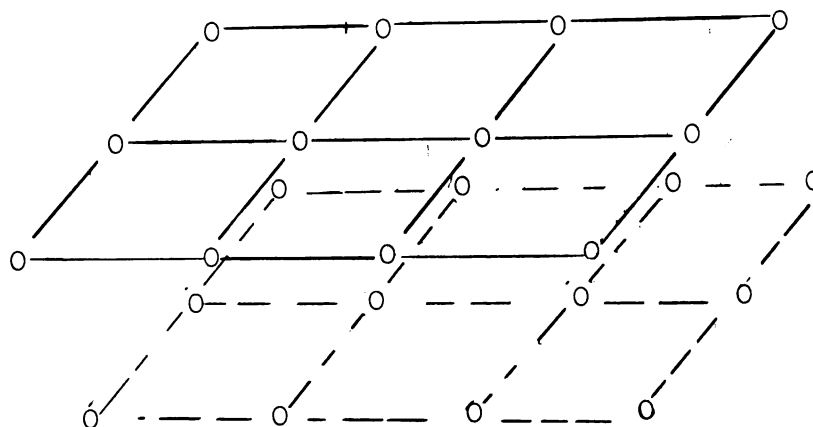
The following three transitions would then be expected: $e \longrightarrow b_1$, $a_1 \longrightarrow b_1$, and $b_2 \longrightarrow b_1$ (Δ). In all four compounds, a band is seen at 14,500-15,700 cm^{-1} . This is either the $b_2 \longrightarrow b_1$ transition or both the $b_2 \longrightarrow b_1$ and $a_1 \longrightarrow b_1$ transitions. Because of this uncertainty, Δ cannot be measured. It should be noted that the band appears at lower energy in the chloride alkoxides than in the alkoxides, in agreement with the fact that chloride is lower in the spectrochemical series than oxygen bonded ligands.

The magnetic data (Table I) for these compounds yields further information as to their structure. Copper (II), having a d^9 configuration, should have a spin-only magnetic moment of 1.72 B.M. However, because of spin-orbit coupling, the experimental moments are usually higher (1.70-2.20 B.M.). Thus in the alkoxides and chloride alkoxides, extensive spin-pairing is indicated by their low magnetic moments.

The spin pairing can be caused by either a super exchange mechanism or by direct overlap of d orbitals of two copper (II) ions. The latter effect is found in copper (II) acetate monohydrate which has a magnetic moment of 1.4 B.M. at room temperature (54). Without x-ray data or knowledge of the variation of the molar susceptibility with temperature, the cause of the low moments cannot be ascertained. It should be noted, however, that the chloride alkoxides have higher magnetic moments than the alkoxides. Oxygen bridges facilitate electron-transfer more than chloride bridges.

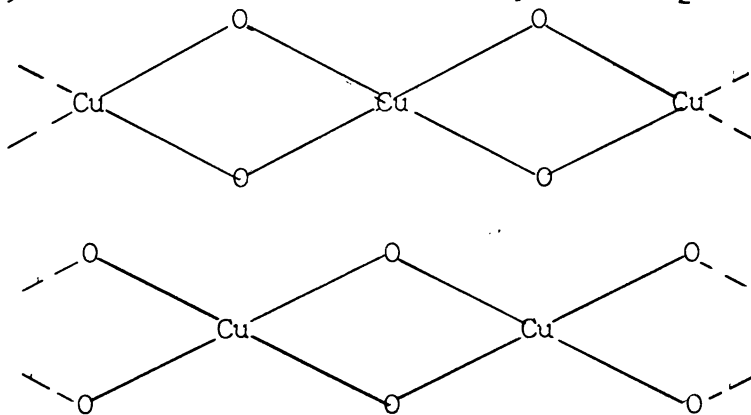
Three different structures for the alkoxides and chloride alkoxides can be proposed, and these will be discussed with respect to the spectra and magnetic properties.

One structure is that of a one-dimensional polymer consisting of staggered hexamer units.



O represents the ligand.

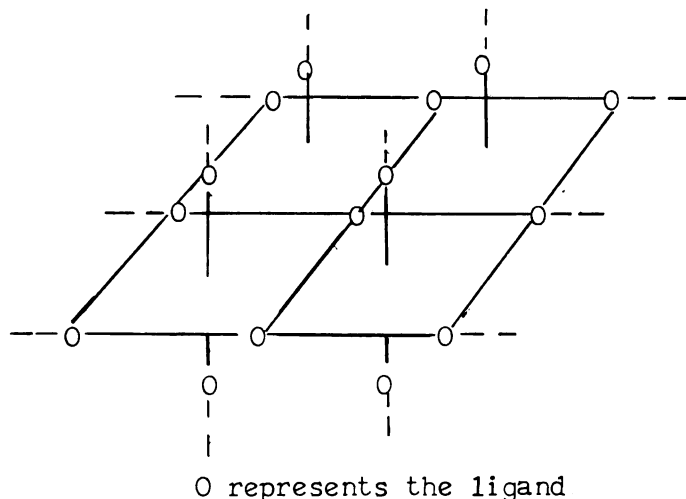
The copper atoms are in a tetragonal environment, but, there is the inherent difficulty that certain of the alkoxide ligands will formally contain seven coordinated oxygen atoms. On that basis, the above structure does not seem likely. Two other structures seem to be more reasonable, of which the first is basically the CuCl_2 structure.



O represents the ligand

Each copper atom has an immediate square planar environment, but also interacts electrostatically with the ligands above and below the plane. In this way there is tetragonal distortion, but in this structure all the ligands are bridging.

Finally, and perhaps the most plausible structure, is that of a three dimensional polymer.



Each copper atom has a tetragonal environment, and there are non-equivalent ligands. The ligands in the *xy*-plane are all bridging, whereas the ligands on the *z*-axis (the axis of distortion) are essentially terminal because of their extended distances from the copper. Hence the copper alkoxides will have both bridging and "terminal" alkoxide groups if the chlorine atoms are on the *z*-axis. This interpretation would readily explain the infrared data.

Mixed Metal Alkoxides

Due to the paucity of information about mixed metal alkoxides, it is very difficult to offer reasons for the failure to form double alkoxides between thallium (I) and iron (III), cobalt (II) and titanium (IV), and iron (II) and titanium (IV). Because Meerwein (29) had prepared many aluminum (III) or zinc (II) double alkoxides, similar double alkoxides should be easily synthesized using metal alkoxides of "amphoteric" character. Hence titanium (IV) and iron (III) were hopefully substituted for aluminum (III), but the reactions were unsuccessful.

In the attempt to prepare these double alkoxides, the new compound iron (III) phenoxide was synthesized in order to study its reaction with thallium (I) phenoxide. This compound, $\text{Fe}(\text{OC}_6\text{H}_5)_3$, has an abnormally high magnetic moment, 9.21 B.M., which indicates there is a ferromagnetic interaction between the iron (III) nuclei or that some ferromagnetic impurity is present.

In attempting to prepare a cobalt (II), titanium (IV) double alkoxide, the complex $\text{Na}_2[\text{Co}(\text{OC}_3\text{H}_7^i)_2\text{Cl}_2]$, first reported by Bartley (30), was synthesized. Bartley, while trying to prepare the analogous cobalt (II), zirconium (IV) double alkoxide, inadvertently isolated this.

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