STUDIES ON THE THIOCYANATO COMPLEXES OF NIOBIUM

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ABSTRACT

The purpose of this study is to investigate the thiocyanato chemistry of niobium (V), especially compounds containing niobium-oxygen bonds. The preparation and properties of such compounds are of particular interest with regard to the type of niobium-oxygen bonding.

Niobium pentachloride and niobium oxytrichloride were prepared and used as starting materials. Reactions between niobium pentachloride and potassium thiocyanate were carried out in the solid state and in ether solutions. Two new complex compounds were prepared. Preliminary characterization of these two derivatives was performed and the results obtained agree with the formulae $K_6[Nb_2O_2(NCS)_{12}]$ and $NbOCl_2(NCS)$, respectively. It has been shown that in thiocyanato-niobium pentachloride systems the niobium-oxygen bond forms in ether solutions. A reaction between niobium oxytrichloride and potassium thiocyanate occurred, resulting in different complex species formation.

The results suggest the chemistry of niobium oxothiocyanato compounds is complex and interesting.

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INTRODUCTION

Thiocyanato complexes of niobium and tantalum are of interest from the following points of view:

1. The type of thiocyanate ligand coordination, which may occur via nitrogen or via sulfur, giving rise to both simple and bridge-bonded structures.

2. The probability of high coordination numbers in ligand spheres involving thiocyanates.

3. The properties of complexes with mixed ligand spheres involving thiocyanato ligands, in particular the existence and properties of oxothiocyanato niobium complexes.

4. The possibility of Nb=O group formation in the complexes prepared from ether solutions.

Recently hexacoordinated niobium(V) thiocyanates have been prepared and the following compounds were reported: $KNb(NCS)_6$, $K_2Nb(NCS)_6$, $[(C_6H_5)_4As]Nb(NCS)_6$ and $(C_4H_9)_4NNb(NCS)_6$ by Brown and Knox;[1,2] $[Nb(NCS)_5]_2$, $Nb(NCS)_5$, $[Nb(NCS)_5(CH_3CN)]$, $[NbCl_4(NCS)(C_2H_5OC_2H_5)]$, $[NbCl_3(NCS)_2(C_2H_5OC_2H_5)]$ and about twenty other complexes and salts of niobium(V) containing thiocyanate ligands by Böhland, Tiede and Zenker;[3,4] $[C_2H_2N_2S_3]_2H[Nb(NCS)_6]$, $[(C_6H_5)_4P]_2[NbO(NCS)_5]$ and $[(C_6H_5)_4As]_2[NbO(NCS)_5]$ by Djordjevic and Tamhina.[5,6]

These studies have raised several points pertinent to the investigations reported in this thesis. Among these are:

1. Stability of $NbO(NCS)_5^{2-}$ salts compared with analogous $Nb(NCS)_6^{-}$ salts.

2. According to infrared evidence, all of the complexes reported seem to be N-bonded isothiocyanates.[1-6]

3. Complexes reported by Böhland and his coworkers,[3,4] prepared from ether solutions of niobium pentachloride, apparently do not contain niobyl groups. From previous observations complex formation with other ligands in ether solution occurs with formation of the Nb=O group.[7] Apparently oxygen is abstracted from ether with subsequent formation of ethyl chloride.

It is our intent to investigate preparations of thiocyanato complexes of niobium, utilizing the reactions of niobium oxytrichloride and niobium pentachloride with potassium thiocyanate in diethyl ether. We hope to determine the effect of oxygen on the coordination number and bonding by the thiocyanate ligands to niobium. In addition we are interested in seeing if niobyl group formation occurs in niobium pentachloride-potassium thiocyanate-diethyl ether solutions.

CHAPTER I

LITERATURE SURVEY

Thiocyanato-Complexes of Transition Metals

Thiocyanato complexes of the transition metals have been of considerable interest in recent years. This interest arises from the fact that the thiocyanate ion can bond to metal atoms in several ways. Much work has been devoted to determining how this group attaches itself to various transition metals. The interpretation of physical properties of these compounds, in order to establish certain criteria for determining bonding by the thiocyanate ligand, has been the subject of extensive studies. Some very interesting trends in bonding by this ligand to transition metals have been discovered, and several explanations for these trends have been extended.

The thiocyanate ligand is ambidentate.[8] Coordination to a metal may therefore occur either through a sulfur or nitrogen atom, or both, leading to several distinct structural types. The ligand may attach itself to a metal atom through the nitrogen end, forming an isothiocyanate, or it may attach itself through sulfur forming a thiocyanate. Finally, the thiocyanate ion may form bridged structures between metal atoms. These bridged structures may be formed either by both the nitrogen and the sulfur bonding to two metal atoms, or by the sulfur atom bridging two metal atoms. Both types of bridging are conceptually possible in the same molecule from a theoretical point of view. The possible bonding types are shown schematically below:

(I)	(II)	(III)	(IV)	(V)
M-S-C≡N	M-N=C=S	M-S-C≡N-M	M-S-M, with C≡N on S	(M)₂S-C≡N-M

Evidence has been obtained from complexes of structures I through IV.[8] X-ray crystallographic studies have definitely established structures I, II, and III.[9,10,11]

In recent studies thiocyanates have been prepared for most of the transition metals. Many of the transition metals have had their thiocyanato chemistry extensively studied and compounds of the class have been fully characterized. In other transition metals, various complexes have been reported, but full characterization is incomplete. A partial listing of the thiocyanato complexes reported is given in Table I, along with the type of bonding encountered in the particular compound.

Inspection of Table I indicates that the first transition series forms nitrogen bonded isothiocyanato compounds almost exclusively. In the second and third transition series the behavior of the metal atoms is somewhat more complex. The

TABLE I

TRANSITION METAL THIOCYANATES

First Transition Series

Element	Compound	Bonding	Reference
V	$(NH_3)V(NCS)_6 \cdot 4H_2O$	V-NCS	12
Cr	$(NH_4)Cr(NH_3)_2(NCS)_4$	Cr-NCS	12,13
	$K_3Cr(NCS)_6 \cdot 4H_2O$	Cr-NCS	12
	$[(C_6H_5)_4N]_3[Cr(NCS)_6]$	Cr-NCS	14
Mn	$K_2Mn(NCS)_4 \cdot 6H_2O$	Mn-NCS	12
	$HgMn(NCS)_4$	Mn-NCS-Hg	16
	$Mn(N_2H_4)_2(NCS)_2$	Mn-NCS	15
Fe	$Fe(py)_2(NCS)_2$	Fe-NCS	13
	$HgFe(NCS)_4$	Fe-NCS-Hg	16
Co	$Co(py)_2(NCS)_2$	Co-NCS-Co	13
	$K_2Co(NCS)_4$	Co-NCS	13
	$[(C_2H_5)_4N]_2[Co(NCS)_4]$	Co-NCS	14
	$CoHg(NCS)_4$	Co-NCS-Hg	17
Ni	$Ni(NH_3)_4(NCS)_2$	Ni-NCS	12,13
	$Ni(py)_4(NCS)_2$	Ni-NCS	12,13
	$[Ni(NH_3)_2(NCS)_4]^{2-}$	Ni-NCS	12
	$Ni(NH_3)_2(NCS)_2$	Ni-NCS	12
Cu	$Cu(py)_2(NCS)_2$	Cu-NCS-Cu	13

TABLE I (Continued)

Zn	$BaZn(NCS)_4 \cdot 2H_2O$	Zn-NCS	13
	$K_2[Zn(NCS)_4] \cdot 4H_2O$	Zn-NCS	8
Second Transition Series			
Nb	$[Nb(NCS)_5]_2$	Nb-NCS-Nb and Nb-NCS	3
	$KNb(NCS)_6$	Nb-NCS	2
	$K_2Nb(NCS)_6$	Nb-NCS	2
Mo	$K_3(Mo)(NCS)_6 \cdot 4H_2O$	Mo-NCS	12
	$Tl_3Mo(NCS)_6$	Mo-NCS	12
Rh	$K_3Rh(SCN)_6$	Rh-SCN	12,3
	$Tl_3Rh(SCN)_6$	Rh-SCN	12
	$Rh(PR_3)_2(SCN)_2$	Rh-SCN-Rh (suspected)	18
Pd	$K_2Pd(SCN)_4$	Pd-SCN	14,12
	$[(C_2H_5)_4N]_2[Pd(SCN)_4]$	Pd-SCN	14
Ag	Ag(SCN)	Ag-SCN-Ag	11
	$[Ag(SCN)_2]^-$	Ag-SCN-Ag and Ag-SCN	11
Cd	$Cd(etu)_2(SCN)_2$		8
	$K_2Cd(SCN)_4 \cdot 2H_2O$	Cd-SCN-Cd and Cd-SCN	12

TABLE I (Continued)

<u>Third Transition Series</u>

Ta	$K\ Ta(NCS)_6$	Ta-NCS	2
	$[Ta(NCS)_5]_2$	Ta-NCS	3
Re	$Re(NCS)_6{}^{2-}$	Re-NCS	19
	$Re_2(NCS)_6{}^{2-}$	Re-NCS-Re and Re-NCS	19
Pt	$K_2Pt(SCN)_4$	Pt-SCN	12,13,14
	$K_2Pt(SCN)_6$	Pt-SCN	12,13
	$Pt(NH_3)_2(SCN)_2$	Pt-SCN	12
Au	$K[Au(SCN)_4]$	Au-SCN	14
	$[(C_2H_5)_4N][Au(SCN)_4]$	Au-SCN	14
Hg	$K_2Hg(SCN)_4$	Hg-SCN	12,13
	$CoHg(SCN)_4$	Hg-SCN-Co	17
	$HgMn(SCN)_4$	Hg-SCN-Mn	16
	$HgFe(SCN)_4$	Hg-SCN-Fe	16

py = pyridine

etu = ethylenethiourea

heavier elements show an increasing tendency to form the nitrogen bonded isothiocyanates. Deviations from these generalizations occur when ligands other than thiocyanate are introduced into the coordination sphere.[8]

In addition to simple sulfur and nitrogen bonded thiocyanates, several compounds have been found in which both ends of the thiocyanate ligand are involved in bonding. These "bridged" compounds may be formed between two atoms of the same element or between atoms of two different elements. Bonds formed by such bridged structures come in a "variety of strengths,"[13] depending on how well the particular end of the ligand can coordinate with the metal atom in question. The most common cases of bridged compounds occur in complexes in which the sulfur atom is bonded to a metal atom. This metal atom normally forms a terminal thiocyanato complex. The nitrogen, furthermore, is bonded to a metal which normally forms a terminal isothiocyanato complex. Also homonuclear bridged structures are more common among elements which normally coordinate with sulfur in terminal thiocyanato complexes.

Several explanations for the behavior of the transition metals with respect to nitrogen or sulfur bonding by the thiocyanate ion have been extended. Various proposals will be discussed below.

The behavior of the transition metals in combining with the thiocyanate ion seems to be closely related to the division of metals into class (a) and class (b) as proposed by Ahrland, Chatt and Davies.[20] This classification is based on the stability constants of ions in solution. Class (a) metals form their most stable complexes with donor atoms belonging to the second short series (i.e., nitrogen, oxygen and fluorine) and class (b) metals form their most stable complexes with donor atoms belonging to the third or subsequent series (i.e., phosphorous, sulfur, chlorine). This classification was expanded by Pearson[21] who has designated class (a) metals as "hard acids" and class (b) metals as "soft acids." Hard acids are defined as atoms or ions with small atomic radii, high effective nuclear charge, low polarizability and a resistance to oxidation. Soft acids are characterized by low positive charge, large size, filled outer orbitals, and high polarizability. From empirical data, observations have led to the conclusion that hard acids tend to coordinate to hard bases (donor atoms of small size and low polarizability). Soft acids tend to coordinate with larger more easily polarizable donor atoms (i.e., sulfur). Among the the possible explanations for this behavior, Pearson mentions the ionic-covalent theory and the pi bonding theory. Other workers have applied these theories to a wide range of systems in transition metal thiocyanates to explain the bonding in this particular class of compounds.

Lewis, Nyholm and Smith[12] used a form of the ionic-covalent theory to explain the bonding in metal thiocyanates.

They stated that "the way in which the (NCS^-) group is bound (i.e., through sulfur or nitrogen) will be decided by the relative bond energies of a covalent metal-sulfur bond and the more ionic metal-nitrogen bond." This statement was based on the assumption that "(a) in the NCS^- ion the lone pairs on the sulfur are more easily polarized than those on the nitrogen atom and (b) the permanent lone pair on the nitrogen atom is larger than that on the sulfur atom." This study considered cases in which the thiocyanate ion was the only ligand present. A semi-quantitative approach and the above assumptions show that small highly charged metal atoms tend to form ionic bonds with the nitrogen end of the thiocyanate ion. Larger ions in lower oxidation states, on the other hand, tend toward covalent sulfur bonds.

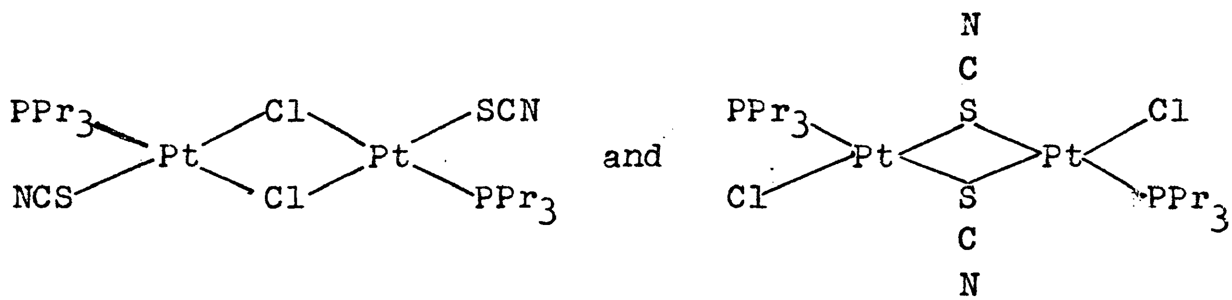
Two other research groups[20,15] favor the pi-bonding theory to explain the bonding between transition metals and thiocyanate ions. The class (b) metals or soft acids possess loosely held d-orbital electrons which can form pi bonds by donation of these electrons to a suitable ligand atom (i.e., sulfur). The contribution of d-pi electrons of the metal to the empty d-orbitals on the sulfur favors stabilization of the metal-sulfur bond. Such stabilization does not occur in nitrogen-bonded isothiocyanates. This theory is supported because sulfur bonding occurs in $[M(SCN)_4]^{2-}$ and $[M(NH_3)_2(SCN)_2]$ where M = palladium or platinum, but nitrogen bonding occurs in $[M(PR_3)_2(SCN)_2]$. Turco and Pecile[15] explain the change from sulfur to nitrogen bonding in complexes of this type by the fact that strong pi electron acceptors, such as tertiary phosphines, can make the d_e orbitals of the metal less available for bonding with the pi-orbitals of the sulfur atom.

Lewis et al. state that nitrogen bonded thiocyanates may be either angular or colinear, but sulfur bonded compounds are always angular. This geometry produces the possibility that steric factors may enter into the determination of bond type. Basolo[22] has shown in palladium and platinum that by introducing bulky substituents into the coordination sphere with only thiocyanate ions, nitrogen bonded complexes are favored. Thus, Basolo has explained that nitrogen bonded complexes are more probable because of greater steric requirements of sulfur bonded compounds.

Infrared Spectra of Transition Metal Thiocyanates

Several workers, investigating infrared spectra of transition metal thiocyanates, have studied all of the various bending and stretching modes present. These workers have empirically assigned various vibrational frequencies to particular modes, depending on how the thiocyanate ion coordinates to the central metal atom. The infrared spectra of this type of compound have been so extensively studied that this method of determining bond type has become an important and widely used diagnostic method.

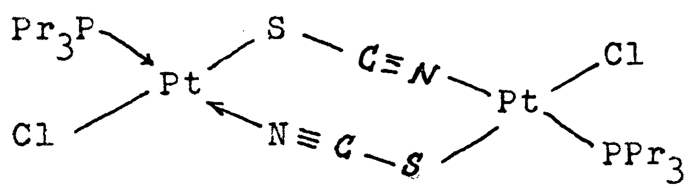
Chatt and a group of co-workers[23,24] in the late 1950's made the first conclusive interpretation of the infrared spectra of transition metal thiocyanates. These scientists were investigating a compound of platinum with the molecular formula $(PPr_3)_2Pt_2Cl_2(SCN)_2$ that exists in two isomeric forms (designated as α and β). These forms had originally been postulated to be structural isomers. The first proposal for the structures is given below:



When these two structures were proposed in 1952,[25] there was no way of discerning the difference.

Using the infrared spectra of the two isomers, Chatt et al. showed that both thiocyanates were bridging in both isomers. This conclusion was arrived at through the examination of the infrared spectra of mononuclear compounds, which could contain only terminal thiocyanates, and through the examination of binuclear compounds which must contain both bridging and terminal thiocyanates on the basis of their composition. The mononuclear compounds show a strong absorption in the range 2100 to 2120 cm^{-1} which was tentatively assigned to the C-N stretching mode. All of the binuclear complexes show two peaks in the range 2100 to 2170 cm^{-1}, one absorption in the range 2100 to 2120 cm^{-1} and the second between 2150 and 2180 cm^{-1}. Based on the above data, bridging thiocyanates exhibit stretching frequencies about 30 to 80 cm^{-1} higher than the corresponding frequencies originating from terminal thiocyanate ligands.

An X-ray crystallographic analysis[24] determined the structure of the α isomer. The structure is shown below.



The X-ray crystallographic study confirmed that infrared spectra are adequate criteria for predicting the presence of bridging thiocyanates.

Mitchell and Williams[13] conducted an extensive study on the structure and bonding of inorganic thiocyanates and on the infrared spectra of these compounds. Their interest in this field was aroused by the fact that in organic thiocyanates and isothiocyanates, the C-N stretching frequency is usually 35 to 80 cm^{-1} higher in compounds of the type R-SCN than in compounds of the type R-NCS.[26] Originally they had hoped to develop a basis for identifying sulfur bonded and nitrogen bonded thiocyanates in inorganic compounds using the C-N stretching frequency. The case of inorganic thiocyanates, however, is not nearly as simple as the case of organic compounds.

Mitchell and Williams investigated the C-N stretching frequencies of a large number of inorganic thiocyanates of known structure. On the basis of this study, several observations are evident. First, when all other factors are constant, the following order of frequencies is observed: M-NCS $<$ M-SCN $<$ B-SCN-M. Secondly, "for a given disposition of the thiocyanate ion, the more polarising the cation (the greater its charge or its electronegativity, or the smaller the cation) the greater the frequency of the C-N vibration . . . and . . . bridged thiocyanates are formed in a variety of strengths."[13] Finally the conclusion was made "that bridging thiocyanates can only be recognized by the infrared spectrum if it is strongly attached at both ends."[13]

Although the C-N stretching is generally at higher frequencies in sulfur bonded thiocyanates than in nitrogen bonded isothiocyanates, this generalization is not without exception. Experimental observations indicate that several factors are responsible for the variability in position of the C-N stretching mode in inorganic thiocyanato complexes. These observations include the following five factors: the coordination and stereochemistry of the complex, the cation used to neutralize the charge on anionic thiocyanato complexes, the valency of the metal atom, the ionic or covalent character of the metal ligand bond, and the angle subtended at the metal atom by the thiocyanate group. On the basis of their observations, these workers decided that the position of the C-N stretching mode could not be used as a conclusive proof for the type of bonding in such compounds.

Lewis, Nyholm and Smith[12] have also studied the infrared spectra of a large number of inorganic thiocyanates in order to determine the type of bonding in several thiocyanato complexes of molybdenum. This group studied the entire infrared spectrum, not just the C-N stretching region. Their results concurred with the previous study: there is an overlap in the C-N stretching region between sulfur and nitrogen bonded thiocyanates. From the position of other bands in the vibrational spectra, however, certain additional correlations could be derived.

Their observations include, primarily, the first overtones of the bending mode of the thiocyanate ligand are generally of about the same intensity as the fundamentals themselves in the isothiocyanates. In the thiocyanates these overtones are usually weaker than the fundamental. Secondly, C-S stretching frequencies seem to fall into two groups. In every case studied, the thiocyanates absorb in the range 694 to 723 cm^{-1}. All isothiocyanates, on the other hand, fall in the range of 760 to 880 cm^{-1}. The authors concluded that the position of the C-S stretching frequency is of greater diagnostic value for determining sulfur or nitrogen bonding than is the C-N stretching frequency. The third observation is "all of the thiocyanates studied show two main C-N bands in the solid state spectra. This factor was not observed for isothiocyanates even at high resolution."[12] Lastly, the bending frequencies are considerably different in the nitrogen and sulfur bonded cases. The nitrogen bonded compounds exhibit a band or bands of medium intensity near 470 cm^{-1}. The sulfur bonded compounds, however, show absorptions at lower frequencies and weaker intensities. Sulfur bonded compounds usually show a wider separation and a greater number of bands in this region of the spectrum.

Turco and Pecile[15] have also concluded that the position of C-S stretching frequency is of great value in determining whether the thiocyanate ion attaches to a metal atom through nitrogen or sulfur. They observed in several compounds studied that thiocyanates absorb between 780 and 860 cm^{-1} and isothiocyanates absorb between 690 and 720 cm^{-1}.

In 1965 Sabatini and Bertini[14] conducted a study on the infrared spectra of some metallic cyanates, thiocyanates and selenocyanates. This work was consistent with the earlier studies in the interpretation of the infrared spectra of metallic thiocyanato compounds. In this study, the bending mode occurs at about 475 cm^{-1} for isothiocyanates, and there is more than one absorption in the range of 400 to 480 cm^{-1} with the most intense band at about 420 cm^{-1} for thiocyanates. These men believe that the position of this bending mode may be used as a criteria for determining sulfur or nitrogen bonding.

Thiocyanato Complexes of Niobium

A wide variety of thiocyanato complexes of niobium have been prepared and characterized over the past few years.[1-6] Knox and Brown[1,2] have prepared salts of the type $MNb(NCS)_6$ and $M_2Nb(NCS)_6$ (where M = K; $(C_4H_9)_4N$; $(C_6H_5)_4As$; and $M_2 = K_2$). The hexathiocyanatoniobium(V) anion is formed according to the following equations.

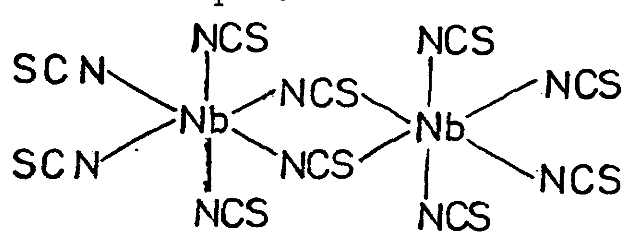
$$NbCl_5 + CH_3CN \longrightarrow NbCl_5 \cdot CH_3CN$$
$$NbCl_5 \cdot CH_3CN + 6KCNS \longrightarrow KNb(NCS)_6(CH_3CN) + 5KCl$$

Because $NbCl_5 \cdot CH_3CN$ and $KNb(NCS)_6(CH_3CN)$ are relatively soluble in acetonitrile and potassium chloride is relatively insoluble, acetonitrile was the solvent used. The difference in solubility allows for the separation and purification of the thiocyanato complex from the potassium chloride produced in the reaction. The preparation of $K_2Nb(NCS)_6$ follows essentially the same scheme. The high sensitivity to moisture of these products necessitated extreme care in all experiments causing all preparations to be involved and complex. In addition, the authors describe the preparation of $[(C_6H_5)_4As]Nb(NCS)_6$ and $(C_4H_9)_4N\ Nb(NCS)_6$.

Infrared spectra are consistent with niobium forming nitrogen bonded isothiocyanates in all four of the compounds prepared. The infrared spectra of $KNb(NCS)_6$ and $K_2Nb(NCS)_6$ in the solid state are very similar, but in acetonitrile solution the two spectra differ. The most intense band of the niobium(V) complex in the C-N stretching region appears at 1981 cm^{-1}. In the niobium(IV) complex, however, the most intense band occurs at 2035 cm^{-1}, a difference of 54 cm^{-1}. The authors believe the lack of d orbital electrons in the niobium(V) complex is responsible for the frequency differences.[2] The presence of one d electron in the niobium(IV) complex explains the C-N absorption in the same range where other studies on transition metal thiocyanates have observed similar stretching modes for nitrogen bonded ligands.

An extensive study of the ultraviolet and visible absorption spectra has led to the same conclusion about bonding in niobium thiocyanates; niobium forms the nitrogen bonded isothiocyanato series.[1,2]

Bőhland <u>et al</u>.[3,4] have thoroughly examined the thiocyanato chemistry of niobium and have prepared and characterized over twenty such compounds. The compound shown below was proposed from one experiment.[3]



The compound was prepared by dissolving niobium pentachloride in acetonitrile and adding ammonium thiocyanate in a mole ratio of five thiocyanates to one niobium. After filtering off the ammonium chloride formed in the reaction and adding benzene to the clear filtrate $[Nb(NCS)_5(CH_3CN)]\cdot 2CH_3CN$ precipitated.

By using thermal and vacuum treatment of the compound formed, the result was a series of products. The method of preparation is shown below.

$$[Nb(NCS)_5(CH_3CN)]\cdot 2CH_3CN$$
$$\Big\downarrow\ 75^{\circ}\text{-}80^{\circ}C,\ 0.3\ \text{Torr}$$
$$[Nb(NCS)_5(CH_3CN)]\cdot CH_3CN$$
$$\Big\downarrow\ 80^{\circ}C,\ 0.3\ \text{Torr}$$
$$[Nb(NCS)_5(CH_3CN)]$$
$$\Big\downarrow\ 110^{\circ}C,\ 0.3\ \text{Torr}$$
$$[Nb(NCS)_5]_2$$

The presence of bridging and of terminal thiocyanate groups is explained on the basis of two strong absorptions in the C-N stretching region (2090 cm^{-1} and 1983 cm^{-1}) and also on the presence of a second less intense band in both the C-S stretching and N-C-S deformation regions. This compound was also examined using ultraviolet and visible spectroscopy and conductivity measurements. The data from these studies are consistent with a dimeric structure.

Böhland _et al._[4] have also reported the preparation of a series of compounds of general formulae :

$$[Nb(Cl)_a(NCS)_b(CH_3CN)]\cdot c(CH_3CN)$$

and $[Nb(NCS)_5(CH_3CN)]$ (where a = 4-1, b = 1-4 and c = 0 or 1) and salts of the type $M[Nb(NCS)_6]\cdot dCH_3CN$ (where M = NH_4^+, K, pyridinium, quinolinium, ½Sr, ½Ba and d = 2; M = Na and d = 5 or 2). Thermal treatment of these compounds leads to solvent free products.

Starting with niobium pentachloride and using either acetonitrile or diethyl ether as a solvent, a series of thiocyanato chloride exchanges can occur. The number of chlorides replaced is dependent upon the molar ratio of niobium pentachloride and ammonium thiocyanate. Böhland and his co-workers prepared and separated the entire series of thiocyanate-chloride exchange products and analyzed them for niobium and thiocyanate only. The salts were prepared by dissolving $[Nb(NCS)_5(CH_3CN)]$ in acetonitrile and then adding the appropriate thiocyanate salt. After filtering the solutions and treating them with benzene, the salts precipitated out. Upon dissolving niobium pentachloride in ether and then adding potassium thiocyanate to the solution $[NbCl_4(NCS)(C_2H_5OC_2H_5)]$ and $[NbCl_3(NCS)_2(C_2H_5OC_2H_5)]$ formed. The ether solution was red. After filtering the solutions and evaporating the solvent, crystalline solids appeared.

Böhland and co-workers also studied $Sr[Nb(NCS)_6]_2\cdot CH_3CN$, $PyH[Nb(NCS)_6]\cdot 2CH_3CN$, $Na[Nb(NCS)_6]\cdot 2CH_3CN$, and $Na[Nb(NCS)_6]$ in order to determine bonding type in these compounds. On the basis of spectral evidence (infrared, ultraviolet, and visible) the conclusion was reached that niobium forms nitrogen bonded isothiocyanato compounds in every case.

The infrared spectra indicate the presence of only terminal nitrogen bonded groups.

In another study,[5,6] Djordjevic and Tamhina prepared the following compounds: $[C_2H_2N_2S_3]_2H[Nb(CNS)_6]$, $[(C_6H_5)_4P]_2$-$[NbO(NCS)_5]$, and $[(C_6H_5)_4As]_2[NbO(CNS)_5]$.

Again all of the compounds were classified as isothiocyanato complexes on the basis of infrared spectra. In this report, Djordjevic and Tamhina assigned the Nb=O stretching frequency to the absorption at 935 cm^{-1}. The remainder of the absorptions fit the criteria for terminal nitrogen bonded complexes. The position of terminal Nb=O bonds in the infrared spectra occur between 890 and 950 cm^{-1} and appear as strong sharp absorptions. Isotopic studies have confirmed this assignment.[27]

TABLE II

THIOCYANATO COMPOUNDS OF NIOBIUM

Compound	Bonding	Reference
$KNb(NCS)_6$	Nb-NCS	1,2
$[(C_6H_5)_4As]Nb(NCS)_6$	Nb-NCS	1,2
$(C_4H_9)_4NNb(NCS)_6$	Nb-NCS	2
$K_2Nb(NCS)_6$	Nb-NCS	2
$[Nb(NCS)_5]_2$	Nb-NCS and Nb-NCS-Nb	3
$Nb(NCS)_5$	Nb-NCS	3
$[NbCl_4(NCS)(CH_3CN)]$		4
$[NbCl_3(NCS)_2(CH_3CN)]$		4
$[NbCl_2(NCS)_3(CH_3CN)]$		4
$[NbCl(NCS)_4(CH_3CN)_2]$		4
$[NbCl_4(NCS)(C_2H_5OC_2H_5)]$		4
$[NbCl_3(NCS)_2(C_2H_5OC_2H_5)]$		4
$NH_4[Nb(NCS)_6]\cdot 2CH_3CN$		4
$K[Nb(NCS)_6]\cdot 2CH_3CN$		4
$K[Nb(NCS)_6]$		4
$Na[Nb(NCS)_6]\cdot 5CH_3CN$		4
$Na[Nb(NCS)_6]\cdot 2CH_3CN$	Nb-NCS	4
$Na[Nb(NCS)_6]$	Nb-NCS	4
$C_5H_5NH[Nb(NCS)_6]\cdot 2CH_3CN$		4

TABLE II (Continued)

$Sr[Nb(NCS)_6]_2 \cdot 4CH_3CN$		4
$Sr[Nb(NCS)_6]_2 \cdot 1CH_3CN$	Nb-NCS	4
$Sr[Nb(NCS)_6]_2$		4
$Ba[Nb(NCS)_4]_2 \cdot 4CH_3CN$		4
$Ba[Nb(NCS)_6]_2 \cdot CH_3CN$		4
$Ba[Nb(NCS)_6]_2$		4
$[(C_2H_2N_2S_3]_2H[Nb(NCS)_6]$		5,6
$[(C_6H_5)_4P]_2[NbO(NCS)_5]$		5,6
$[(C_6H_5)_4As]_2[NbO(NCS)_5]$		5,6

CHAPTER II

EXPERIMENTAL SECTION

Manipulations with moisture sensitive materials were carried out in a Vacuum Atmosphere Corporation glove-box (Model HE-43-2) with a molecular sieve drying train (Model HE 493).

Purification and Drying of Chemicals

Aluminum Trichloride: Baker Reagent Grade aluminum trichloride was used after sublimation at 180°.

Niobium Pentoxide: City Chemical of New York niobium pentoxide (99.7%) was used as obtained or reprecipitated from a potassium hydrogen sulfate melt. The reprecipitation was accomplished by fusing niobium pentoxide with reagent grade potassium hydrogen sulfate in a platinum crucible. The clear melt was cooled and then dissolved in hot oxalic acid (10% by weight). To the clear, cooled oxalic acid solution ammonium hydroxide (7.5 N) was added until hydrous niobium oxide precipitated. The precipitate was centrifuged and washed twice with ammonium nitrate (2%). The freshly precipitated hydrous niobium oxide was dried at 600°C.[29]

Potassium Thiocyanate: Prior to use, Fisher Reagent Grade potassium thiocyanate was dried at 70° for 24 to 48 hours.

Acetonitrile: Fisher Certified Grade acetonitrile was distilled from phosphorous pentoxide.[30]

Acetone: Fisher High Grade acetone was distilled from phosphorous pentoxide and stored over molecular sieves 4A .

Benzene: Fisher Reagent Grade benzene was dried over sodium until there was no further evolution of hydrogen gas.

Diethyl Ether: Fisher Reagent Grade diethyl ether was dried over sodium before use.

Tetrahydrofuran: High Grade tetrahydrofuran from Fisher Scientific was found to contain peroxides after testing with acidic potassium iodide. The tetrahydrofuran was distilled from cuprous chloride (0.3% by weight) to remove peroxides. It was then redistilled from lithium aluminum hydride.[32]

Petroleum Ether: Fisher petroleum ether was dried by storing over molecular sieves 4A and used without further treatment.

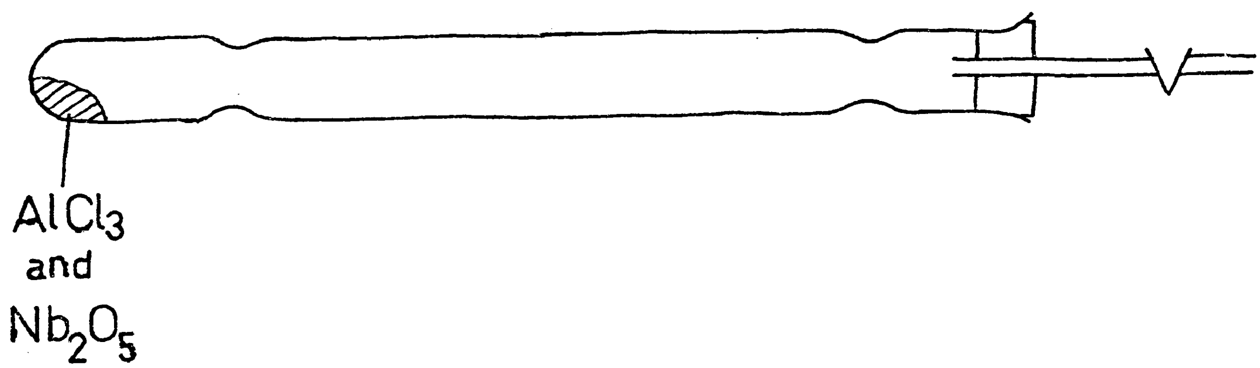
Preparation of Niobium Oxytrichloride and Niobium Pentachloride

Niobium oxytrichloride was prepared using two[33,34] different techniques. It was impossible to obtain large quantities of pure niobium oxytrichloride by either method. Niobium pentachloride was a side product in one of the preparations of the oxytrichloride. The first preparation of niobium oxytrichloride was based on the reaction

$$Nb_2O_5 + 2AlCl_3 \xrightarrow{240^\circ} 2NbOCl_3 + Al_2O_3 \qquad (33)$$

The stoichiometry of the reaction required approximately equal weights of aluminum trichloride and niobium pentoxide. The preparations were carried out in sealed evacuated glass reaction tubes at a temperature of 240°C.

The preparation was first attempted using the reaction vessel shown below.



The procedure called for the finely ground and thoroughly mixed reactants to be placed in the lower section of the reaction tube. The tube was evacuated using the stopcock at the open end. The tube was then sealed under vacuum at the constriction next to the stopcock. The sealed tube was heated at 240°C for 24 to 48 hours. Following this heating process, the tube was cut at the lower constriction. This procedure allowed for the separation of the aluminum oxide and the unreacted starting material from the middle section, which contained niobium oxytrichloride and niobium pentachloride.

The first problem arose in trying to determine a satisfactory method of heating the vessel to 240°C for long periods of time. A Briskheat heating tape was wrapped around the lower portion of the tube and calibrated. Voltage fluctuations necessitated the use of a Sola constant voltage transformer. Furthermore, the heating tape was also wrapped with asbestos cord. Even with these precautions, the temperature control was no better than $\pm 10^{\circ}C$.

Preparations were attempted using a variety of conditions. First, different thicknesses and sizes of glass tubing were used. These differences had little effect on the yield of niobium oxytrichloride, except when thick walled tubing of small bore was used. In this case yellow niobium pentachloride formed in large quantities just above the reactants. The niobium pentachloride blocked the tube, preventing the reaction from going to completion. Secondly, the temperature was varied from 180° to $260^{\circ}C$. However, $240^{\circ}C$ gave the best results. Thirdly, the ratio of aluminum trichloride and niobium pentoxide was varied from a slight excess of niobium pentoxide to a slight excess of aluminum trichloride with little change in results. Finally, niobium pentoxide was reprecipitated with the intent of making it more reactive. The use of freshly precipitated niobium pentoxide in this preparation did not noticeably change the yield of niobium oxytrichloride. The yield was not improved by carrying out the reaction in tubes which were not evacuated.

In all preparations using the first method, fine yellow crystals of niobium pentachloride were the major product recovered. Several preparations did yield some chunks of white niobium oxytrichloride, which were mechanically separated from the niobium pentachloride. The yields were usually low. The analysis of niobium oxytrichloride showed Nb = 42.84% (Theoretical 43.16%). Because the first procedure gave relatively poor results, a second method was initiated.

A technique described by Brauer[34] was modified to employ the available supply of glassware for constructing a reaction vessel. In this preparation molecular oxygen was passed over niobium pentachloride heated to 150°C. The equation for the reaction is

$$2NbCl_5 + O_2 \xrightarrow{150^\circ} 2NbOCl_3 + 2Cl_2$$

The reaction was carried out in a vessel illustrated in Figure 1. In this preparation, niobium pentachloride was placed in the first section of the reaction vessel, and dried glasswool was inserted into the second section. The first and second sections were wrapped in a heating tape and insulated with asbestos cord. Oxygen was passed slowly through the system (rate can be determined by a gas bubbler) and the first two sections were heated. The niobium pentachloride in the first section vaporized slowly and was carried to the section containing glass wool. Oxygen gas carried the niobium oxytrichloride to the cool third section where it collected on the glass surface. Any niobium pentachloride carried to the

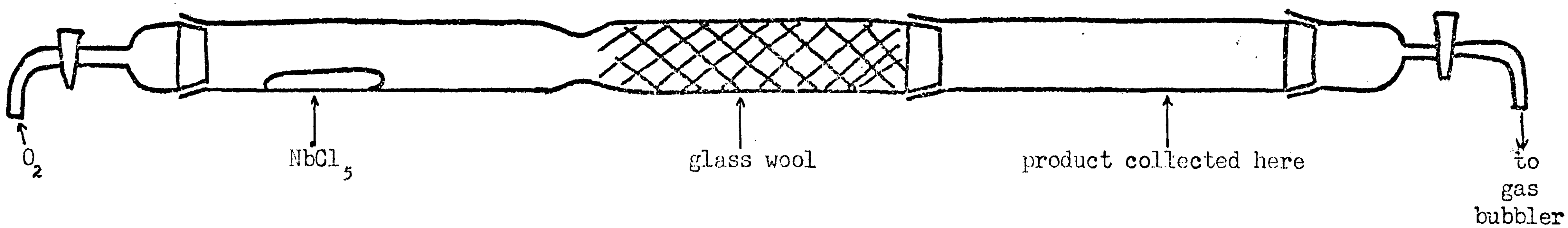
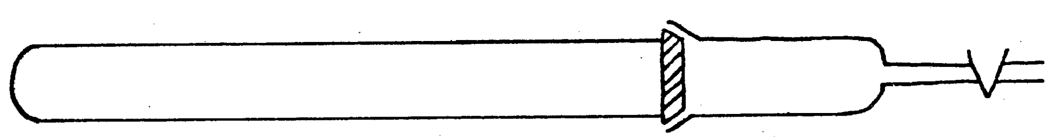


FIGURE 1

APPARATUS FOR THE CONVERSION OF NIOBIUM PENTACHLORIDE TO NIOBIUM OXYTRICHLORIDE third section could be forced back by cuting off the flow of oxygen and then by heating this section with a bunsen burner.

Using a similar apparatus described by Fairbrother,[35] the conversion of niobium pentachloride to niobium oxytrichloride should be complete in about two hours. The attempts to prepare niobium oxytrichloride using the apparatus described above were unsuccessful. At very slow rates of oxygen flow, no product was carried to the collection section. When the rate of flow of oxygen was increased enough to carry the vapors forward, niobium pentachloride was deposited in large quantities. Even when the niobium pentachloride was forced back into the first two sections and oxygen was again passed through the system, a large excess of niobium pentachloride deposited in the final section. A faster flow of oxygen carried some solid material into the oil bubbler, even when the final section was being cooled with acetone soaked towels. After several unsuccessful attempts, this procedure was also abandoned.

Finally, the first procedure was modified to insure better control of the temperature and to simplify handling of the reactants and products. A vessel as shown below was constructed. The reactants were placed in the bottom of the



tube, and the tube was evacuated. After the reaction was completed, the vessel was opened in the dry box. Breaking glass and handling opened reaction vessels in the air was avoided.

To better regulate the temperature of the reaction, the heating tapes were replaced with a silicon oil bath. A Precision Scientific relay and probe were used to control the temperature. The system used is shown in Figure 2. This system held the temperature within the interval 230° to 240°C for long periods of time. A thermometer could be used to check the temperature in the oil bath; whereas, it was impossible to check the temperature in the preparations utilizing the heating tape. This technique gave improved yields of niobium oxytrichloride, but even here the amount of niobium oxytrichloride was low. Again niobium pentachloride was the major product. The analysis of niobium oxytrichloride from this preparation is: Nb = 41.20% (Theoretical 43.16%). The apparatus described on page 30 was also used in an attempt to separate niobium oxytrichloride from the mixture of oxytrichloride and pentachloride. The mixture was placed in the bottom of the vessel, evacuated, and heated to 150° to 160°C to further effect separation. This method was only partially successful in depositing a small quantity of white niobium oxytrichloride from the mixture before yellow niobium pentachloride began to sublime.

None of the attempts to prepare pure niobium oxytrichloride were completely successful. All of the preparations

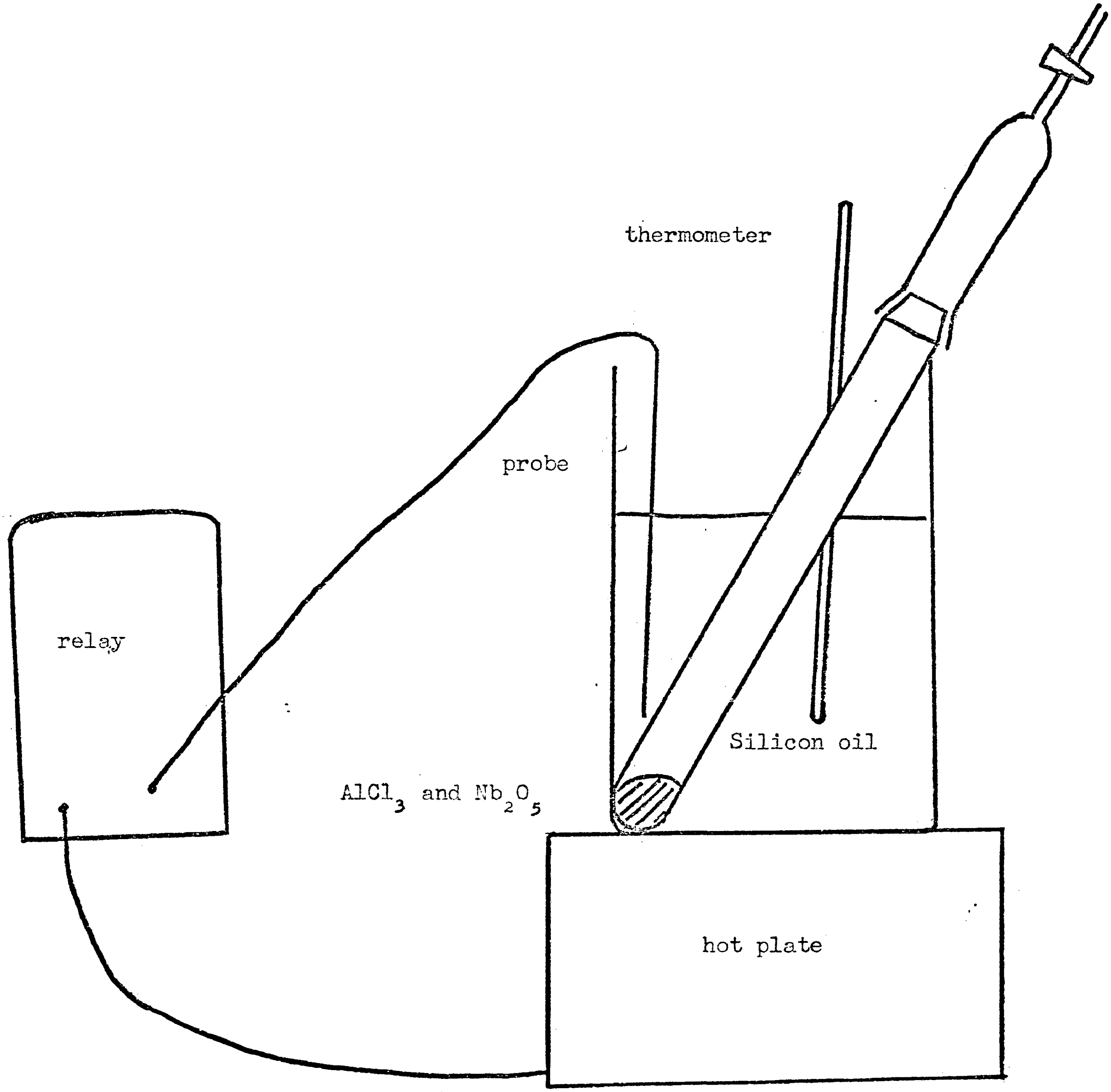


FIGURE 2

REACTION VESSEL FOR THE PREPARATION OF NIOBIUM OXYTRICHLORIDE FROM ALUMINUM TRICHLORIDE AND NIOBIUM PENTOXIDE yielded a mixture of niobium oxytrichloride and niobium pentachloride, with the latter usually in excess. Yellow $NbCl_5$ crystals analyzed as Nb = 34.1% (Theoretical 34.4%)

Nb = 34.3%

Cl = 65.3% (Theoretical 65.6%).

Cl = 65.2%

Preparation of Thiocyanato Complexes

Reaction of Niobium Pentachloride and Potassium Thiocyanate in the Solid State: To check for a reaction between niobium pentachloride and potassium thiocyanate in the solid state, these two chemicals were ground together for five minutes in an agate mortar. The result, a dark orange-brown color, indicated that a reaction did occur.

Reactions of Niobium Thiocyanate with Potassium Thiocyanate in Diethyl Ether: After dissolving niobium pentachloride (0.5 - 1.0g; 2 - 4 x 10^{-3} moles) in diethyl ether (40 ml), the solution was refluxed for one to two hours, returned to the drybox and filtered immediately. To the freshly filtered solution, potassium thiocyanate (3 moles of KCNS per mole $NbCl_5$) was added. Solid products formed, and were extracted with suitable solvents.

The above procedure was attempted several times. In all cases, the dissolution of niobium pentachloride in ether resulted in a yellow or yellow-orange solution which did not change color on refluxing. Immediately upon addition of potassium thiocyanate a dark orange solution resulted. The solution stood for several hours and was stirred occasionally.

These solutions were filtered and light orange solids were obtained. The solids decomposed at about 175°C.

The orange solids were tested for solubility in acetonitrile, acetone, benzene, diethyl ether, chloroform and tetrahydrofuran. The solids were reasonably soluble in acetone and acetonitrile. Acetone was chosen as the solvent for extraction of the compound.

The orange solids were extracted with 30 to 40 ml. portions of acetone. The resulting yellow solutions were filtered and the extraction procedure repeated. To the clear yellow acetone solutions, dry petroleum ether was added gradually with agitation, until a precipitate formed. The addition of petroleum ether was continued until the precipitate became heavy and flocculent. Faint yellow products (Compound I) were collected by filtration and dried. Six preparations were carried out.

The ether filtrates from two of these preparations were left undisturbed for several days in the drybox. Crystalline solids formed in both of these solutions. In one case these crystals were light orange (Compound II). In the other ether solution dark red-brown crystals were obtained in a very small amount.

Reaction of Niobium Oxytrichloride with Potassium Thiocyanate: Due to the low yields of niobium oxytrichloride, few of these preparations were attempted. On mixing and grinding dry, solid niobium oxytrichloride with dry, solid potassium thiocyanate an immediate reaction occurred; the two white solids yielded yellow orange solid. After extraction with ether or benzene the solutions were orange.

In the drybox atmosphere niobium oxytrichloride (0.61g) and potassium thiocyanate (0.83g) were mixed (one mole $NbOCl_3$ per three mole KCNS) and finely ground in an agate mortar for approximately five minutes. The appearance of a yellow orange color resulted almost as soon as the grinding process was begun. Ether was added and a dark orange solution was obtained. The orange solution was decanted and a light yellow solid was left in the flask to dry. In about 48 hours the light yellow solid had turned dark orange-brown. In the ether solution some new yellow crystals formed which were separated from the solution by decantation.

Several other preparations were attempted using ether, benzene, tetrahydrofuran and acetonitrile as solvents, but there were no appreciable yields of products. In every case an orange solid formed in the solid state, but attempts to isolate a pure product were unsuccessful using solvents other than ether.

Analysis of Compounds

Niobium was determined gravimetrically and weighed as Nb_2O_5. Two different procedures were used for the determination.

Procedure 1:[36] About 70 mg of compound was treated with concentrated hydrochloric acid (1 ml) and to the resulting clear solution 25 ml of 5% oxalic acid was added. The solution was diluted to 50 ml and heated to boiling. Niobium was precipitated from the solution by adding ammonium hydroxide (7 M) dropwise. The solution was again heated to boiling and digested for one hour, and then cooled and filtered. The precipitate was washed twice with approximately 10 ml portions of cold 2% ammonium chloride. The precipitate was ignited at 900°C to constant weight.

Procedure 2:[37] The sample (about 50 mg) was dissolved in concentrated sulfuric acid (1 ml) and to the resulting clear solution 5% oxalic acid (25 ml) and water (25 ml) were added. The solution was heated on a steambath. Freshly prepared 2% tannic acid (10 ml) was added and the solution was heated to boiling. Ammonium hydroxide (4 M) was added until the pH was approximately 5.5 as determined by pH paper. An orange flocculent precipitate was obtained which was digested at about 100°C for one hour. The precipitate was filtered, washed with 2% ammonium chloride, ignited to constant weight at 900°C, and weighed as Nb_2O_5. Chloride determinations of the starting material ($NbCl_5$) were conducted potentiometrically, using a Fisher Accumet Potentiometer and standardized $AgNO_3$.

Carbon, Hydrogen, Nitrogen, Sulfur and Chloride analyses of the products were performed by Schwarzkopf Microanalytical Laboratories.

Physical Methods

Infrared Spectra: Infrared spectra of all compounds were taken using a Perkin Elmer Model 427 Infrared Spectrophotometer. All samples were run in Nujol mulls using potassium bromide cells. All mulls were prepared in the drybox using Nujol dried over molecular sieves 4 Å .

Coulometric Analyses: Compound I and Compound II were found to produce acidic solutions when dissolved in water. In order to determine the number of equivalents of hydronium ions produced in aqueous solution per mole of niobium, coulometric tetrations on samples of these niobium compounds were performed. A Leeds and Northrup Model Number 7960 Coulometric Analyzer and a Radiometer pH meter were employed for these analyses.

Weighed samples were dissolved in 50.00 ml of water, containing 0.74 g of reagent grade potassium chloride. The tetrations were carried out in 100 ml tall form beakers. The cell employed for the analyses is depicted in Figure 3.

The coulometric analyzer reads micro-equivalents of hydroxide ions produced in the solution directly. The pH-meter was standardized using Fisher Scientific Buffer Solution (pH - 7.00 ± 0.02). The pH of the solutions was recorded as the number of micro-equivalents of OH ion was increased. Nitrogen gas was bubbled through the solution to stir the solution and prevent carbon dioxide from dissolving in the solution.

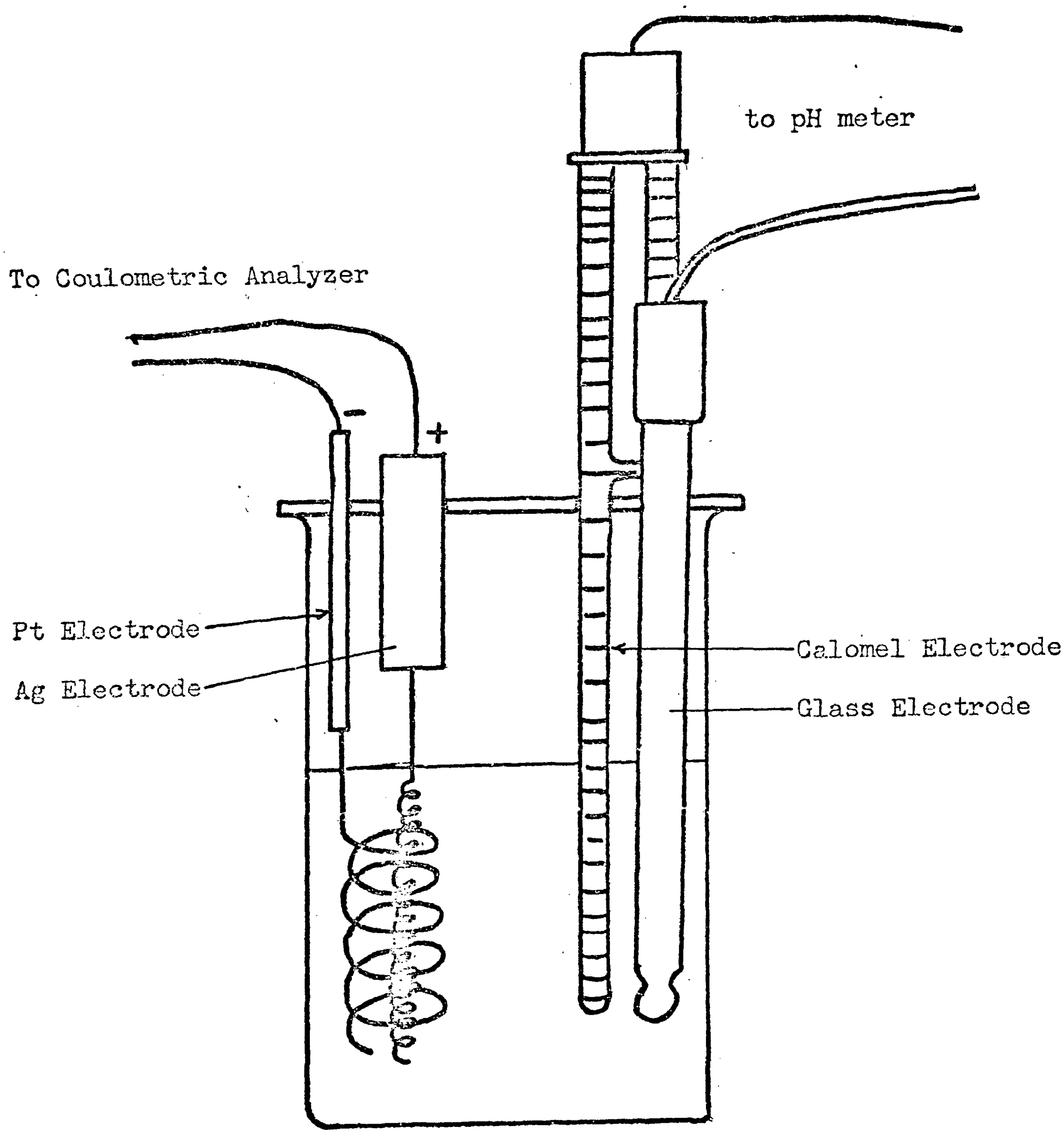


FIGURE 3

COULOMETRIC TITRATION CELL

CHAPTER III

RESULTS AND DISCUSSION

I. Reactions of Potassium Thiocyanate with Niobium Pentachloride

Reaction in the Solid State

A reaction occurred between niobium pentachloride and potassium thiocyanate in the solid state. When these two chemicals were ground together in an inert atmosphere, an immediate color change occurred. This reaction was probably due to a thiocyanate-chloride exchange. Böhland reports such exchange reactions in solution.[3] No further attempt was made to characterize this system.

Reaction in Ether

On dissolving niobium pentachloride in dry diethyl ether the reactions

$$NbCl_5 + Et_2O \longrightarrow NbCl_5 \cdot Et_2O$$
$$NbCl_5 \cdot Et_2O \xrightarrow[\text{heat}]{} NbOCl_3 + 2EtCl$$

are expected to occur.[7] The above reactions should be kept in mind in attempting to understand products obtained from the interaction of potassium thiocyanate and niobium pentachloride in ether.

Potassium thiocyanate was added to ether solutions of niobium pentachloride which had been heated to reflux. The reaction mixture was filtered, leaving an orange solid (Solid I). This solid was dried and a preliminary study was conducted. Solid I decomposed at about 175°C. The infrared spectra (4000-400 cm^{-1}) of Solid I and of potassium thiocyanate as mulls in Nujol are illustrated in Figures 4 and 5. Comparison of these spectra indicates that several absorptions appear in the spectrum of orange Solid I which do not appear in the spectrum of potassium thiocyanate. Notable among these new absorptions are the peaks at 935 cm^{-1} and a broad peak at 745 cm^{-1}, with a shoulder at 720 cm^{-1}. The band at 935 cm^{-1} is in the region of Nb=O stretching frequencies and suggests the presence of this group.

The absorptions in the C-N region are rather broad and poorly resolved, indicating the possibility that unreacted potassium thiocyanate may be present in orange Solid I. Thus this solid was subjected to several purification procedures.

<u>Compound I Prepared from Acetone Solutions</u>

Due to the apparent solubility of the orange solid in acetone, attempts were made to extract the niobium-thiocyanate compound from any potassium thiocyanate. To the filtered yellow acetone extract, dry petroleum ether was added. The result was a pale yellow solid (Compound I), which turned pale tan after drying under vacuum for sixteen hours. Compound I decomposed between 168° and 170°.

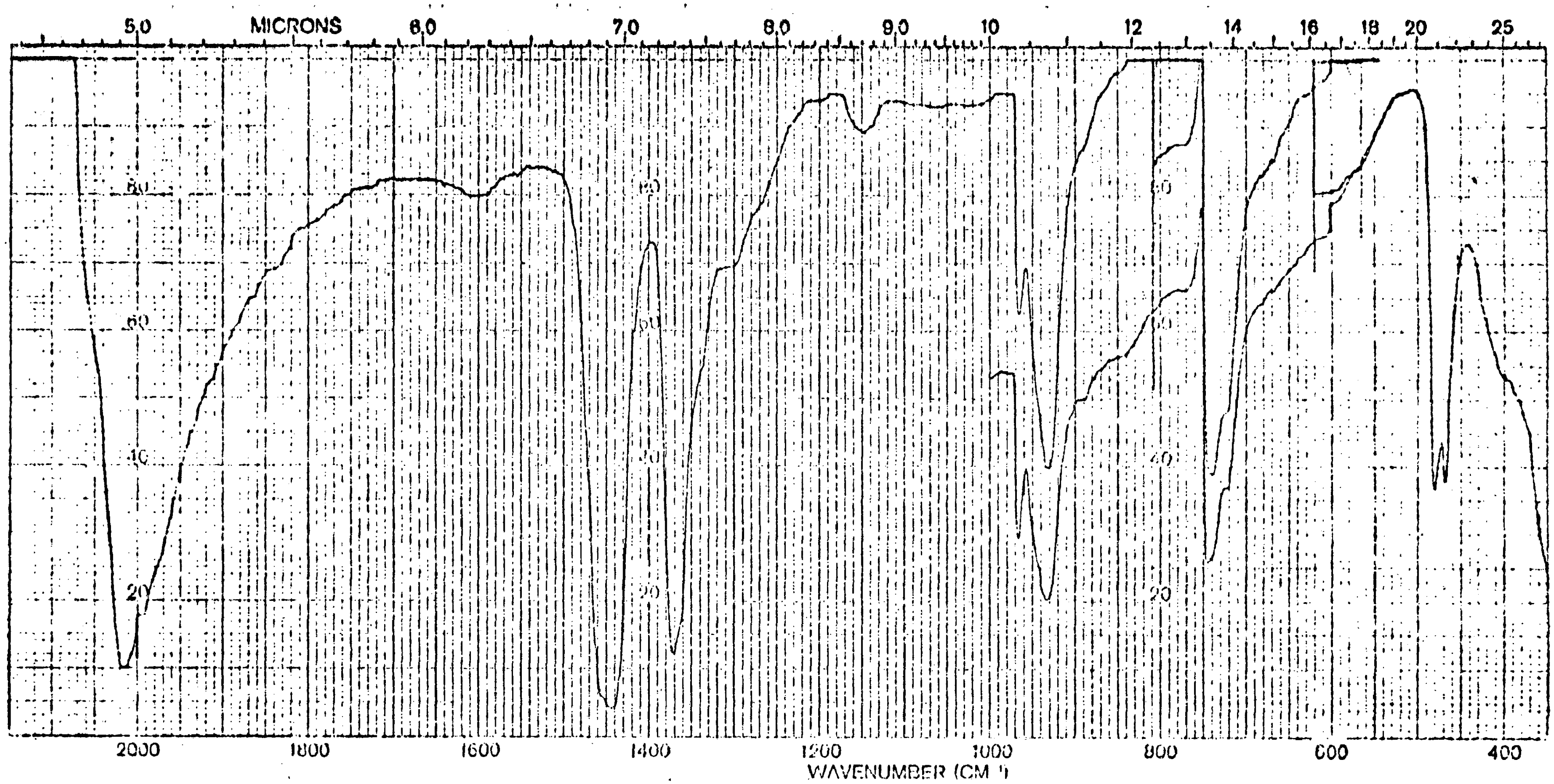


FIGURE 4

INFRARED SPECTRUM OF SOLID I

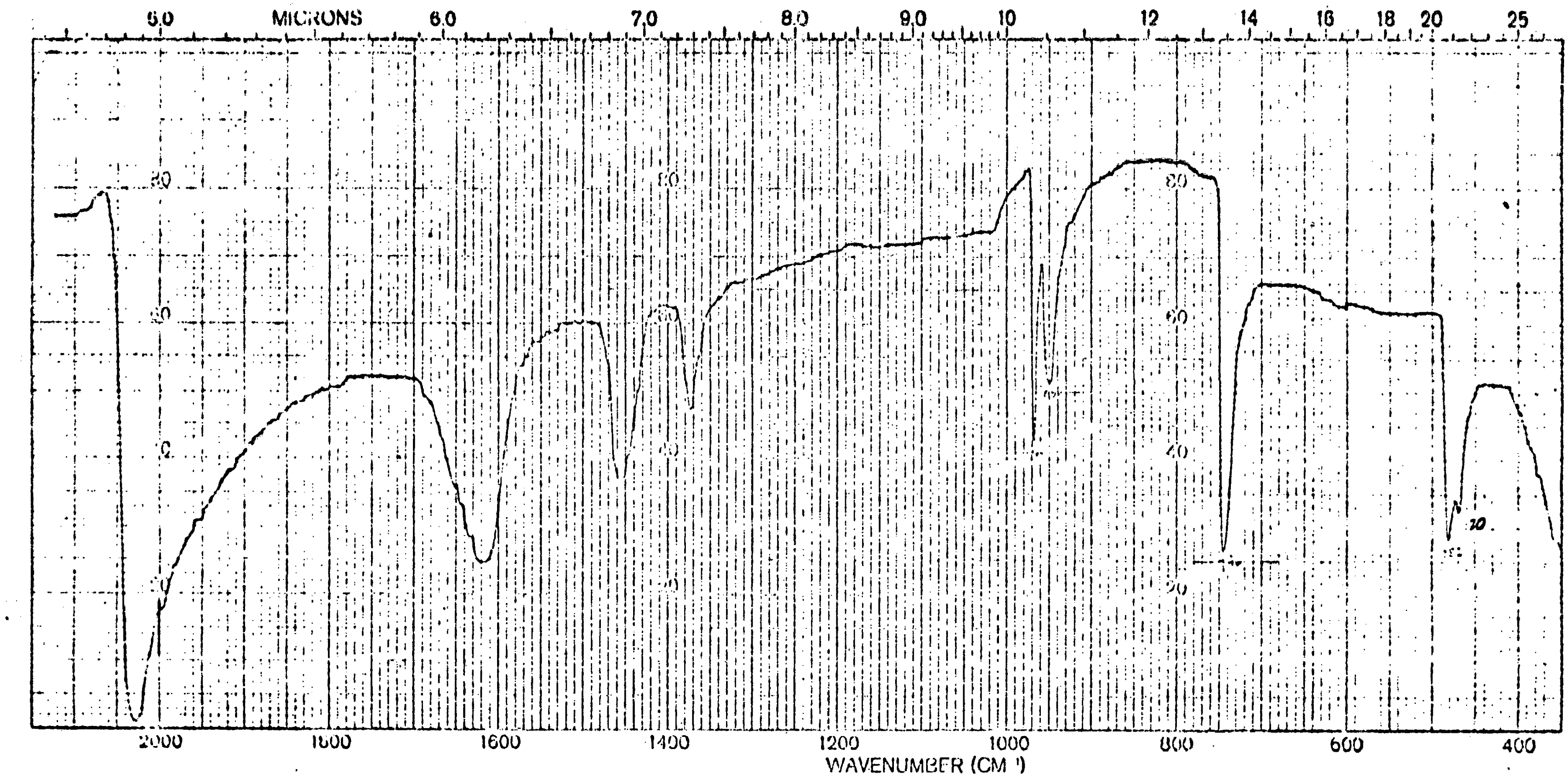


FIGURE 5

INFRARED SPECTRUM OF POTASSIUM THIOCYANATE

The reaction of potassium thiocyanate and niobium pentachloride in ether solution was repeated several times. In every case an orange solid was recovered from the ether solution. Subsequent extractions with acetone yielded identical products (Compound I) as determined from infrared and melting point data.

Compound I analyzed as shown in Table III. The results correspond best with the formulae $K_3NbO(CNS)_6$ or $K_6Nb_2O_2(CNS)_{12}$.

TABLE III

Element	Per Cent Found	Mole Ratic	Expected for $K_3NbO(CNS)_6$
Nb	15.9; 15.4	1	16.1
C	13.31	6.5	12.5
H	0.57		
N	13.57	5.7	14.6
S	28.93	5.3	33.3
Cl	0.87		

The carbon, nitrogen, and sulfur analyses are not completely accurate. The percentage of thiocyanate calculated on the basis of nitrogen and sulfur analyses are not in agreement. The fact that nitrogen and sulfur equivalents are lower than that of carbon is accountable. The infrared spectrum shows traces of acetone, which could not be removed, even after extensive drying. Potassium was not quantitatively determined, but was qualitatively found to be present. Compound I was obtained by precipitation and dried at room temperature under vacuum.

Hydrolysis of $K_6[Nb_2O_2(NCS)_{12}]$ is expected to be a complex process. According to a simple equation:

$$K_6[Nb_2O_2(NCS)_{12}]+6H_2O \longrightarrow \langle 2NbO(OH)_3 \rangle aq.+12NCS^-+6K^++6H^+$$

this compound is expected to give three moles of hydronium ions per mole of niobium. However, coulometric titration shows that 0.38 moles of hydronium ions are released per mole of niobium, indicating that bridging thiocyanates do not hydrolyze quantitatively and the product of hydrolysis is a charged complex niobium species. The titration curve is given in Figure 6.

The infrared spectra in Figures 7 and 8 of Compound I show some interesting features. The terminal Nb=O absorption present in the orange Solid I (Figure 4) has disappeared and an additional strong absorption occurs at 2124 cm^{-1}. This peak is considerably higher than the C-N stretching frequencies reported[1-6] in the previous studies of thiocyanato complexes of niobium. As reported by Chatt,[24,24] et al. absorptions at high frequencies in the C-N stretching region are characteristic of S-N bridging thiocyanates. Böhland reports a compound[3] which he considers to contain bridging thiocyanates, with a frequency at 2080 cm^{-1}. The appearance of a strong absorption at 2124 cm^{-1} in the spectrum of Compound I (Figure 8) strongly indicates that, in Compound I, more than one type of thiocyanato group are present. The absorption at 2045 cm^{-1}

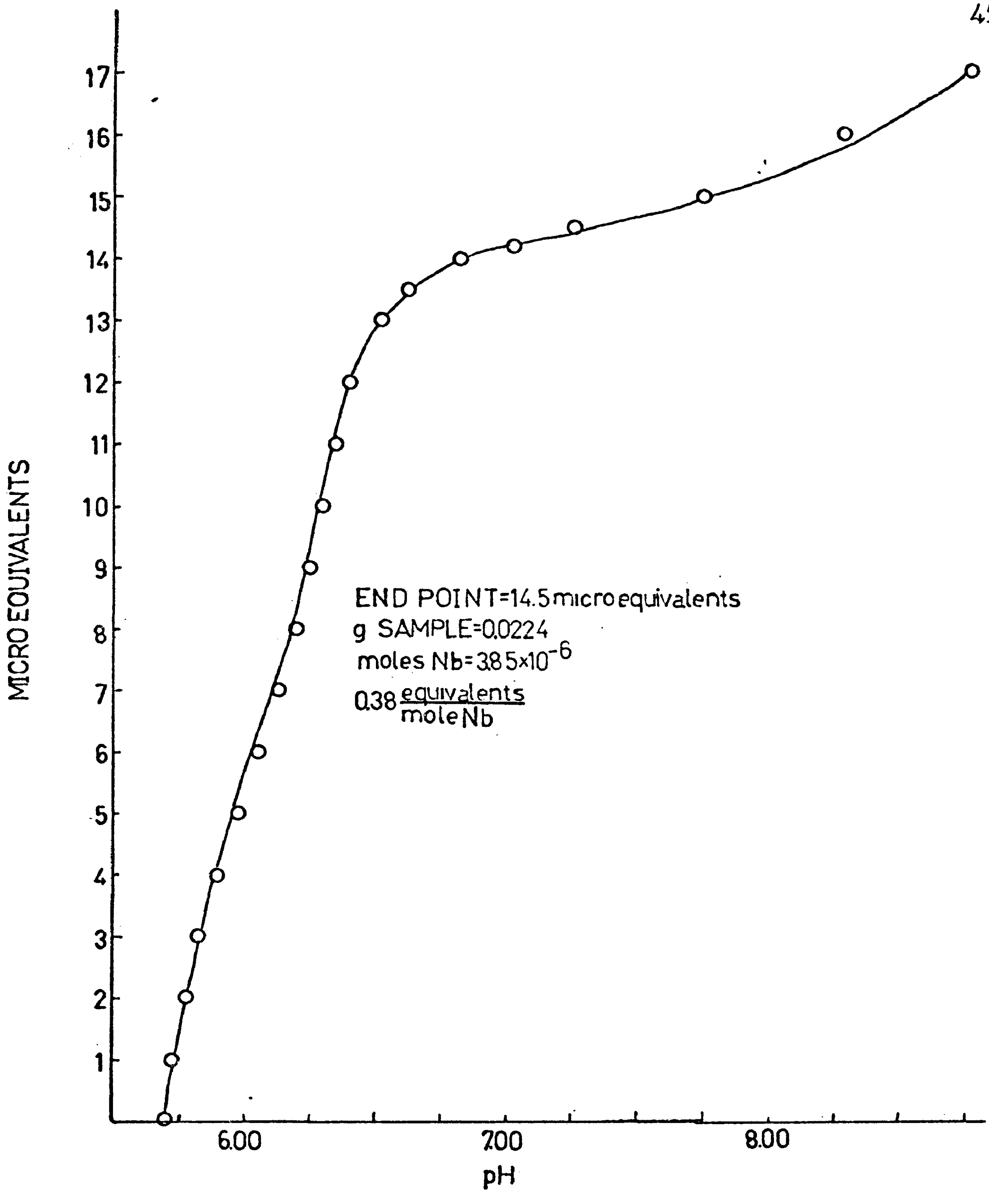


FIGURE 6

COULOMETRIC TITRATION CURVE OF COMPOUND I: $K_6Nb_2O_2(NCS)_{12}$

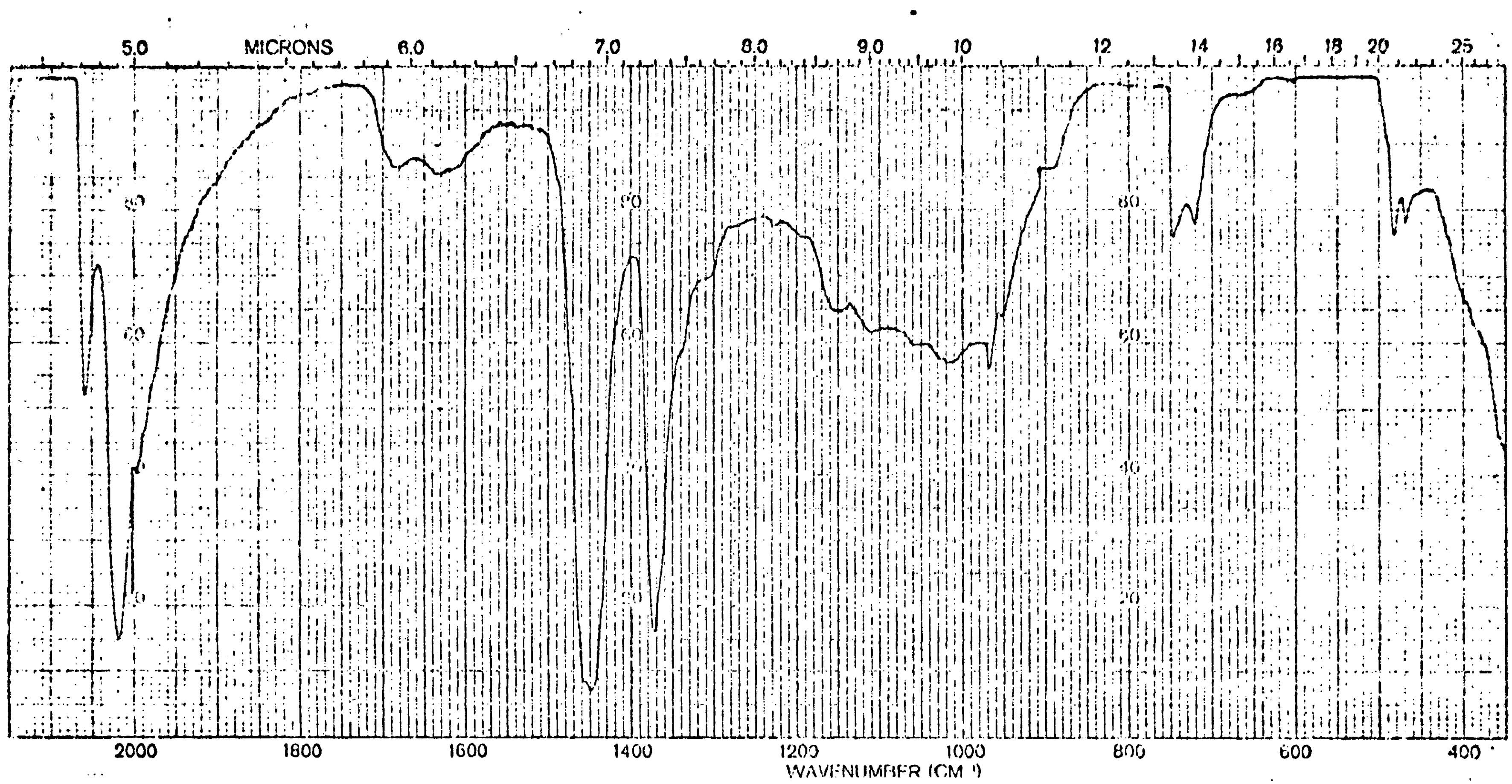


FIGURE 7

INFRARED SPECTRUM OF COMPOUND I (before drying)

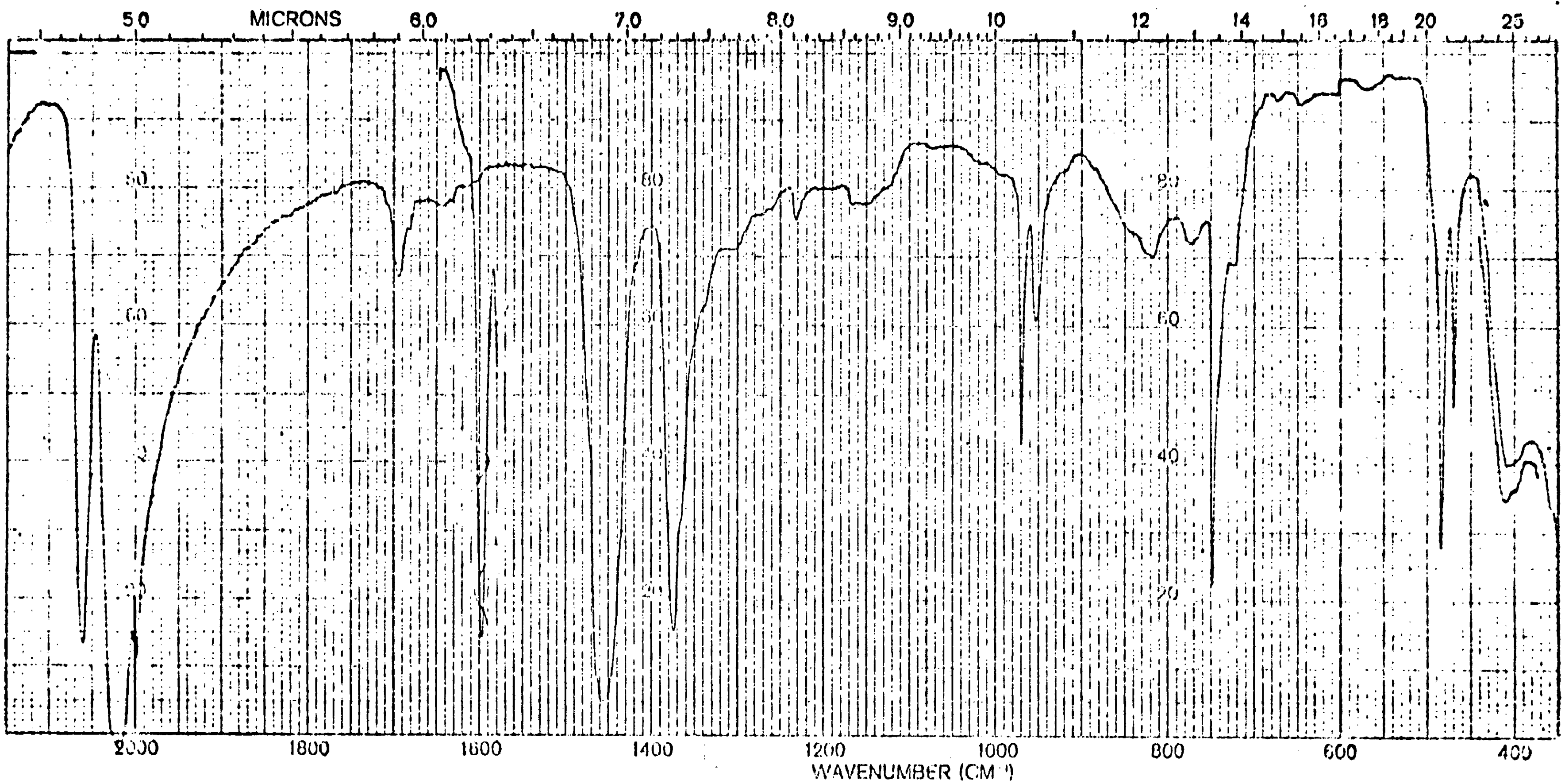


FIGURE 8

INFRARED SPECTRUM OF COMPOUND I (dried)

is characteristic of terminal isothiocyanates.

Another indication of the presence of bridging thiocyanates in Compound I is the strong absorption in the region of the C-S stretching mode at 751 cm^{-1}. In the N-C-S bending region of the spectrum, peaks at 487 and 473 cm^{-1} indicate nitrogen bonded isothiocyanates. The absorption at 413 cm^{-1}, furthermore, is characteristic of sulfur bonded thiocyanates. Here again the presence of bridging and terminal nitrogen bonded thiocyanato groups is supported.

Bridging Nb-O-Nb groups usually show strong broad absorptions between 770 and 850 cm^{-1}.[27] In the spectrum of Compound I, medium intensity absorptions appear at 775 and 820 cm^{-1}. These absorptions may be due to niobium-oxygen bridges. The relatively low intensity may result from the presence of several thiocyanato ligands in the coordination sphere of the niobium(V) .

Compound II Prepared from Ether Solution

Orange crystals formed from the ether filtrate left from the niobium pentachloride-potassium thiocyanate ether system. These orange crystals, formed in the ether filtrate after standing undisturbed for several days, are distinctly different from the orange Solid I. This compound (Compound II) melted at 80°C. There was no apparent change in color after the crystals were dried under vacuum for sixteen hours at room temperature.

The niobium, carbon, hydrogen, nitrogen, and sulfur analyses were performed only once due to the small amount of product available. This data, along with the theoretical values of two possible formulae, are given in Table IV.

TABLE IV

Element	Per Cent Found	Mole Ratio	Expected for $NbOCl_2(NCS)\cdot(C_2H_5)_2O$	Expected for $NbOCl_2(NCS)\cdot 0.5(C_2H_5)_2O$
Nb	33.3	1	29.78	33.79
C	13.81	3.2	19.24	13.10
H	3.69	3.7	3.23	1.83
N	6.44	1.3	4.49	5.09
S	10.64	1	10.27	11.66
Cl			22.73	25.79

The difference in the mole ratio of sulfur and nitrogen suggest that the analysis is not accurate. Since thiocyanate ions from potassium thiocyanate are the only source of either element, the mole ratio of these two elements must be identical. The formulae that best fit the analytical data are:

$NbOCl_2(NCS)\cdot(C_2H_5)_2O$ or $NbOCl_2(NCS)\cdot 0.5(C_2H_5)_2O$

These formulae are speculative since only one analysis was made and since no chloride determination was performed. Insufficient sample size precluded the chloride determination. Drying under vacuum at room temperature partially removed some of the ether molecules from the compound. This may account for some discrepancies observed in the analysis.

Another fact which supports the formula of Compound II is the coulometric analysis. A compound with the formula $NbOCl_2(NCS)$ would be expected to produce, upon hydrolysis, three moles of hydronium ions for every mole of niobium. A value of 2.85 was determined for this product which is close to the expected value of three. The titration curve is produced in Figure 9.

The infrared spectrum of Compound II is given in Figure 10. In the C-N stretching region, absorptions appear at 2095 and 1997 cm^{-1}. In contrast to Compound I, no peaks appear above 2100 cm^{-1} suggesting that no bridging thiocyanates are present. The absorption at 2095 cm^{-1} is probably due to nitrogen bonded isothiocyanato groups. In addition to several bands originating from ether vibrations, there is also a strong absorption at 927 cm^{-1} which can be tentatively assigned to terminal Nb=O stretching. The C-S stretching and N-C-S bending deformation modes appear at 772, 500 and 488 cm^{-1} respectively, which are characteristic of nitrogen bonded isothiocyanates. The spectrum indicates that Compound II contains terminal nitrogen bonded thiocyanato groups, Nb=O group and a coordinated ether molecule.

Solid II Prepared from Ether Solution

Finally, to demonstrate the complexity of the systems studied, the following observation is of interest. From a second niobium pentachloride-potassium thiocyanate-ether

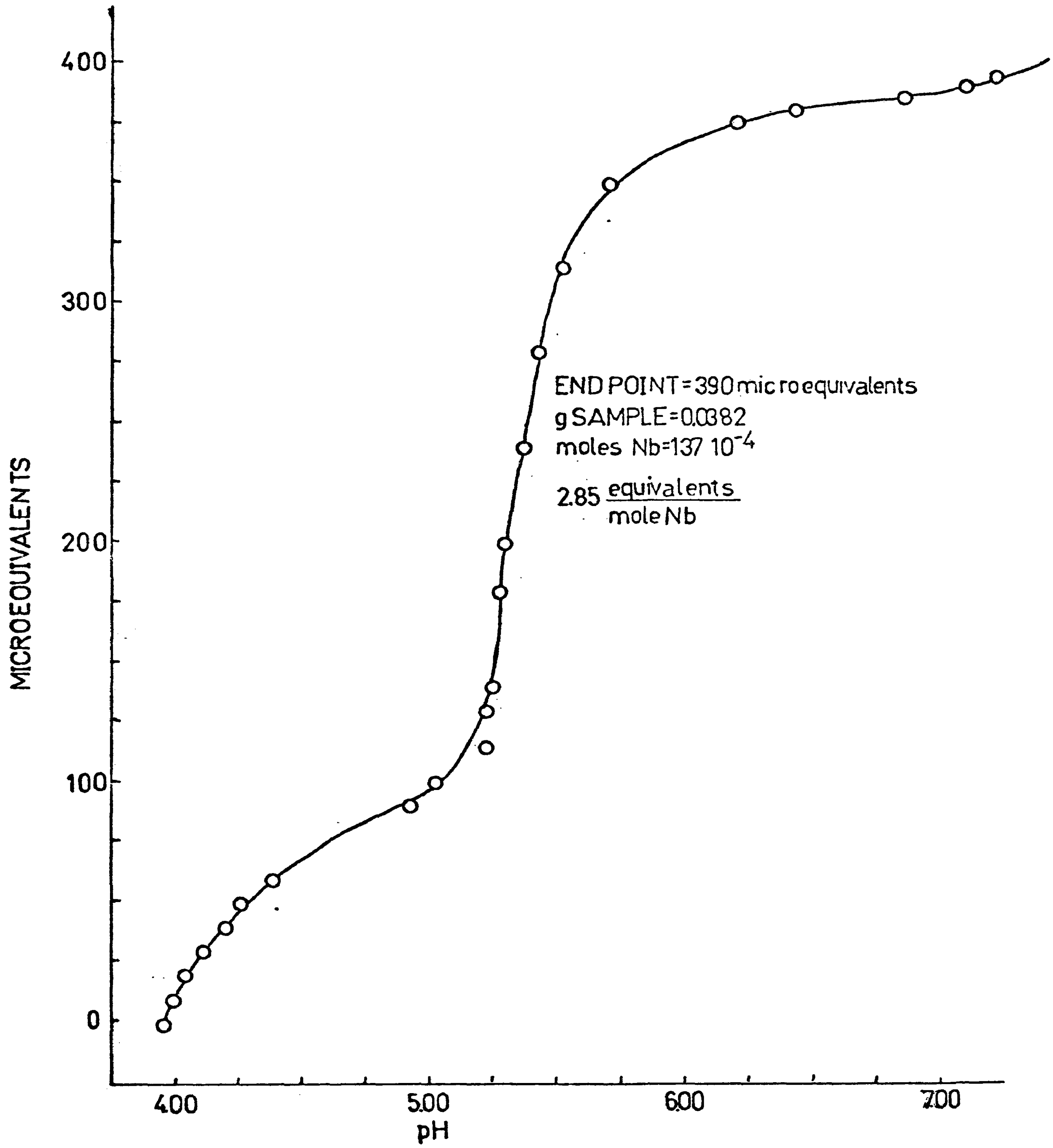


FIGURE 9

COULOMETRIC TITRATION CURVE FOR COMPOUND II: $NbOCl_2(NCS)$

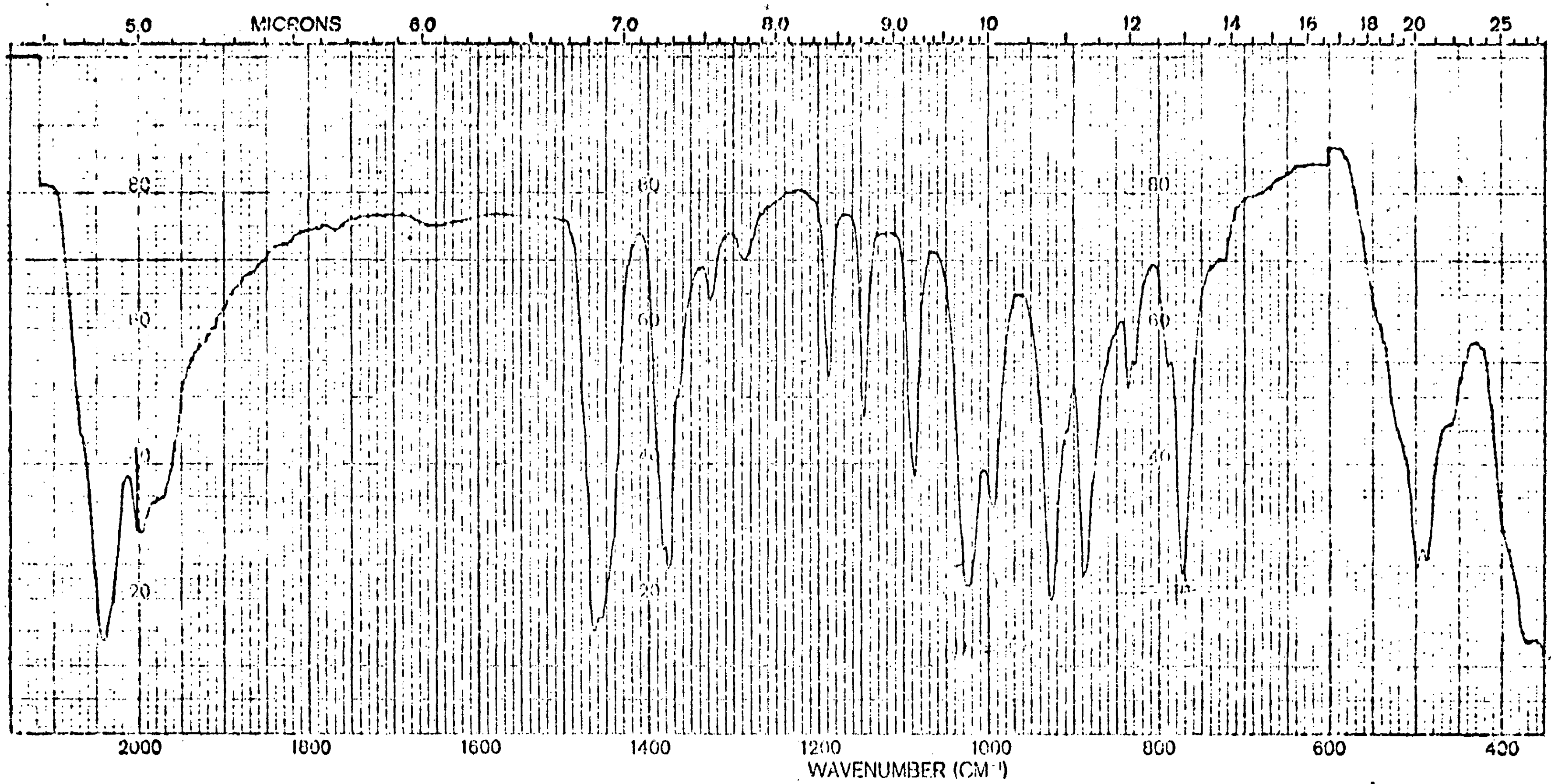


FIGURE 10

INFRARED SPECTRUM OF COMPOUND II

filtrate, a small quantity of red crystals formed in a manner similar to Compound II. The infrared spectrum of this substance (Solid II) is not well resolved, but still contains useful information. There is a strong sharp absorption at 2085 cm^{-1} and a very broad absorption centered at 1950 cm^{-1}. The spectrum differs from that of Compound II, indicating the sensitivity of the C-N stretching mode to the coordination sphere of the central metal atom. The presence of a strong absorption at about 928 cm^{-1} also indicates the formation of a terminal Nb=O bond in ether solutions. The infrared spectrum of Solid II is given in Figure 11.

II. Reactions of Potassium Thiocyanate with Niobium Oxytrichloride

When niobium oxytrichloride and potassium thiocyanate (both white solids) are ground in the solid state a thiocyanate-chloride exchange reaction occurs. A yellow solid results which dissolves in diethyl ether giving a yellow solution. The solution yields a yellow crystalline solid (Solid III) upon evaporation of the solvent. This solid appears extremely unstable, since it turns to a dark red-brown solid (Solid IV) after two days in a drybox atmosphere. The infrared spectra of the yellow crystalline solid and the darker amorphous solid given in Figures 12 and 13 indicate some structural features of the complex.

The yellow solid shows an absorption in the C-N stretching region at about 1960 cm^{-1}, which is characteristic of

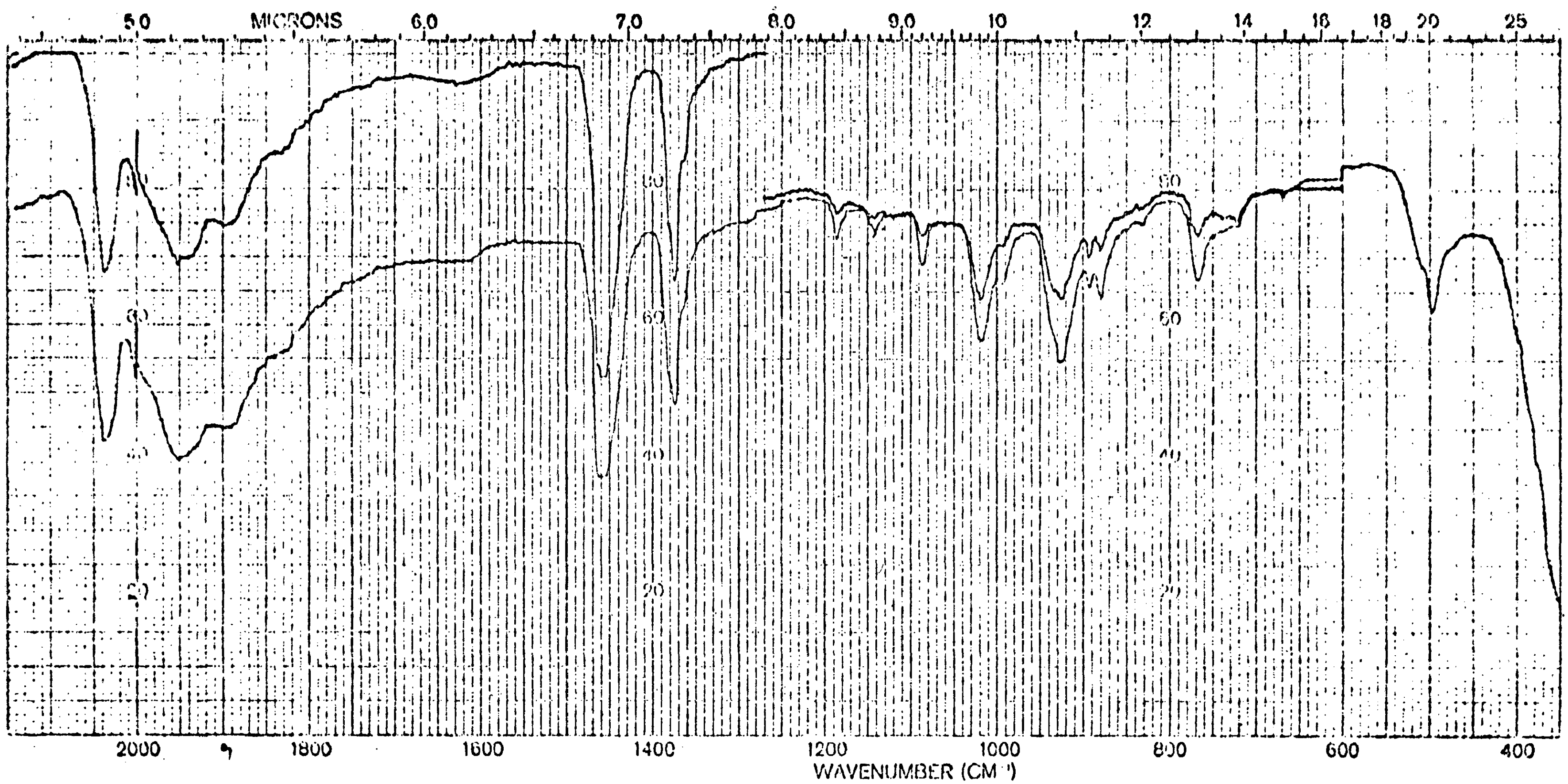


FIGURE 11

INFRARED SPECTRUM OF SOLID II

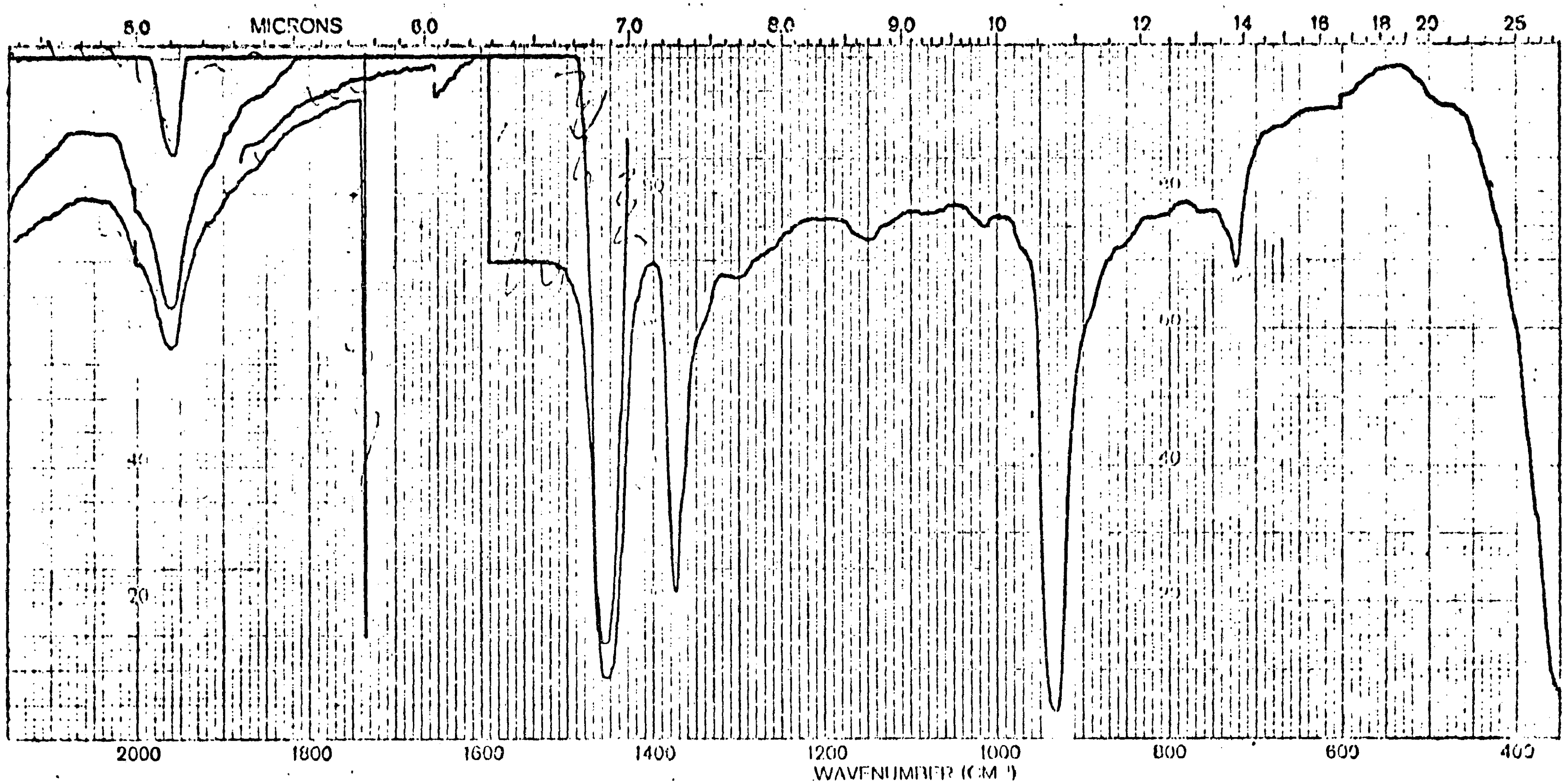


FIGURE 12

INFRARED SPECTRUM OF SOLID III

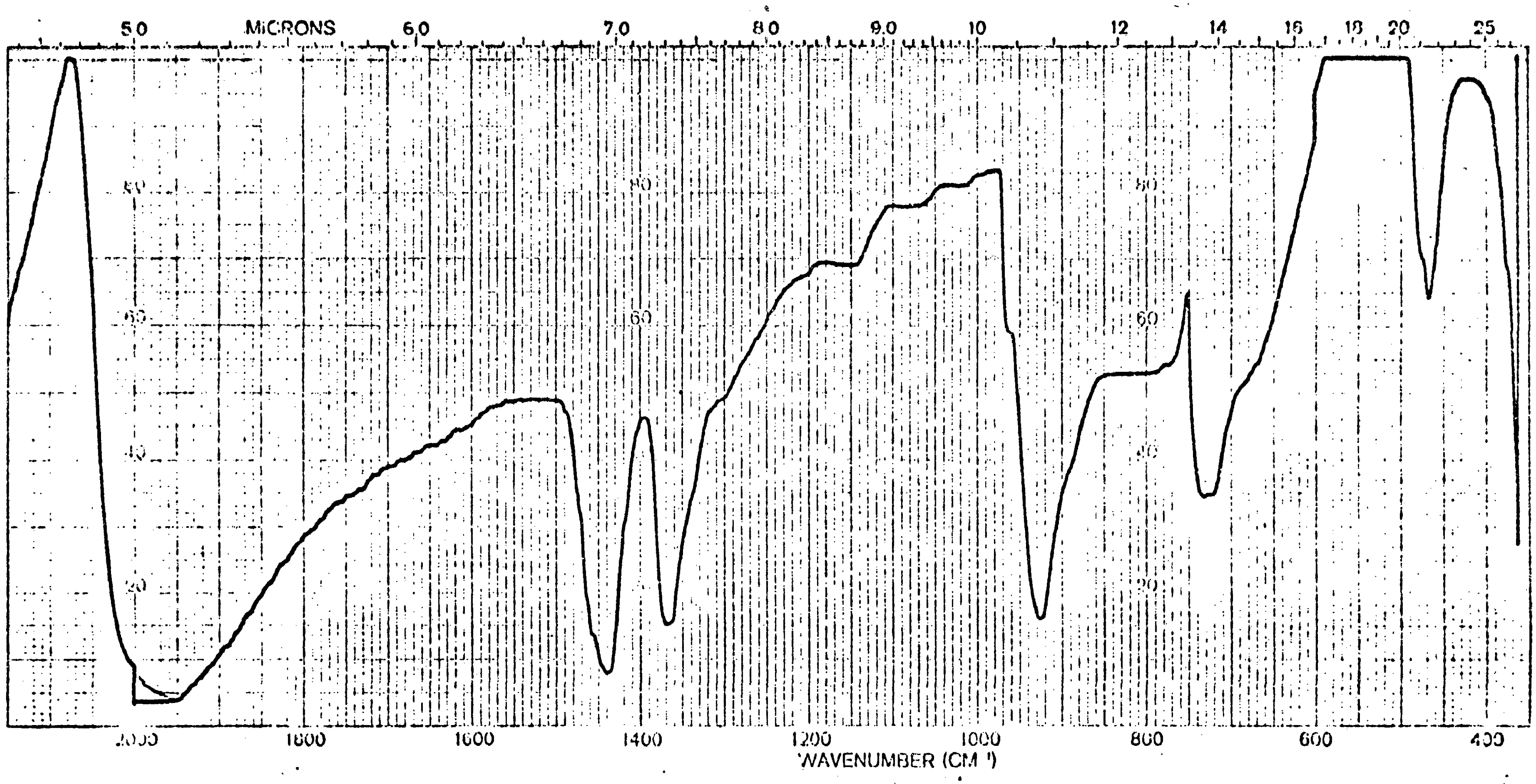


FIGURE 13

INFRARED SPECTRUM OF SOLID IV

a terminally nitrogen bonded thiocyanate ligand. A very strong absorption appears in the Nb=O stretching region at 935 cm^{-1}. The spectrum suggests that metal oxygen bridging does not occur in this compound. A monomeric species containing nitrogen bonded thiocyanato groups and a Nb=O group is probably formed. It is notable that thiocyanate exchange with chloride in niobium oxytrichloride destroys the existing Nb-O-Nb bridges, since in the spectrum there is no absorption between 750 and 880 cm^{-1}. The spectra of the yellow and brown substances indicate a considerable rearrangement in the yellow oxothiocyanato complex. The appearance of a broad intense absorption in the C-N stretching region is indicative of potassium thiocyanate. This is probably due to the decomposition of the oxothiocyanato complex. This interpretation is supported by the appearance of peaks at 730 and 470 cm^{-1}, which are also characteristic of potassium thiocyanate. There is still an absorption at 935 cm^{-1}, but the intensity relative to the C-N absorption has decreased considerably.

On the basis of the infrared spectra it appears as though the oxygen bridges in niobium oxytrichloride are broken in the ether-thiocyanate solution. Furthermore, terminal Nb=O bonds are formed along the Nb-NCS bonds. Further studies are necessary to characterize these derivatives.

The results discussed in this thesis have allowed us to derive some conclusions about the thiocyanato chemistry of niobium. Niobium-oxygen bond formation occurs on refluxing ether solutions of niobium pentachloride. This fact is supported by the existence of niobium-oxygen bond in products prepared from niobium pentachloride in ether (Compounds I and II and Solids I and II). Secondly, a niobium compound involving bridging thiocyanato ligands (Compound I) shows the expected C-N for bridging thiocyanato group above 2100 cm^{-1} and involves a coordination number larger than six. Thirdly, based on infrared spectral evidence, niobium oxygen bridges in niobium oxytrichloride are broken on thiocyanate-chloride exchange in ether solutions. The result is the formation of a terminal niobyl group.

TABLE V

SIGNIFICANT GROUP FREQUENCIES IN THE INFRARED (cm^{-1})

Spectrum of	C-N Stretching	C-S Stretching	NCS Bending	NCS Bending over Tone	Nb=O Stretching	Nb-O-Nb Stretching	O-H Stretching
Solid I	2035(s)	746(s) 722(sh)	469(s) 480(s)	965(s)	932(s)		
KCNS (wet)	2055(s)	746(s)	470(s) 482(s)	950(s) 969(s)			1620(s-br)
$K_6Nb_2O_2(NCS)_{12}$ (with acetone)	2124(m) 2044(s)	749(m) 720(m)	470(m) 485(m)				
$K_6Nb_2O_2(NCS)_{12}$ (dried)	2124(s) 2045(s)	751(s)	487(s) 473(m) 413(m)	973(m) 955(m)		775(w) 822(w)	
$NbOCl_2(NCS)\cdot C_2H_5OC_2H_5$	2090(s) 1997(s)	772(s)	500(s) 488(s)		927(s)		
Solid II	2075(s) 1950(s-br)	767(w-m)	499(m)		925(m)		
Solid III	1962	723			935(s)		
Solid IV	1950(s-br)	735(s-br)	469(m)		925(s)		

FOOTNOTES

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