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METAL-METAL BONDS AND PHYSICAL PROPERTIES OF SOME NICKEL AND PALLADIUM COMPLEXES

by

Dennis Warren Barnum

A Dissertation Submitted to the
Graduate Faculty in Partial Fulfillment of
The Requirements for the Degree of
DOCTOR OF PHILOSOPHY

Major Subject: Analytical Chemistry

Approved:

Signature was redacted for privacy.

In Charge of Major Work

Signature was redacted for privacy.

Head of Major Department

Signature was redacted for privacy.

Dean of Graduate College

Iowa State College
1957

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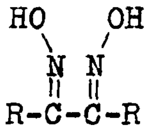
I. INTRODUCTION

A. Purpose of Research

In recent years a great deal of work has been done studying the physical and chemical properties of organic chelating agents. For the analytical chemist the ultimate goal of this work is to be able to design new organic analytical reagents that will give a quantitative color or precipitation reaction with a desired metal ion but will not give interfering reactions with other ions that might be present. Such a reagent is said to be *specific*, while one that will react with several metals but under various conditions is said to be *selective*.

One of the most highly selective organic analytical reagents is the *vic*-dioxime group, I, which precipitates



$$\begin{array}{c} HO \quad OH \\ \backslash \quad / \\ N \quad N \\ \| \quad \| \\ R{-}C{-}C{-}R \end{array}$$

I. a *vic*-dioxime

nickel(II) from weakly acid, neutral, or slightly alkaline solutions, and palladium(II) from moderately acidic solutions (25) according to the reaction (82)

$$M^{++} + 2\ DH_2 = \underline{M(DH)_2} + 2\ H^+ .$$

In this reaction M^{++} represents a metal ion and DH_2 represents a vic-dioxime.

This reaction was discovered in 1905 by L. Tschugaeff (82) who used it to prepare a number of vic-dioxime complexes of transition metals. He reported that the nickel(II), palladium(II), and platinum(II) complexes are insoluble in water, whereas other complexes are soluble. In 1907, in a series of papers, Brunck (13, 14, 15) proposed a method for the gravimetric determination of nickel(II) based on the insolubility of its complex with 2,3-butanedionedioxime. Since then this method has been extensively applied and it has proved so convenient and free from interferences that today many of the methods for the determination of nickel involve the use of a vic-dioxime.

In the last few years it has been shown that the selectivity of the vic-dioxime group is due to the ability of its complexes to pack in the crystal in such a way that chains of weak intermolecular metal-metal bonds are formed (36). The metal-metal bonds in this type of packing contribute enough stability to the crystal that it is insoluble in water, and the unique packing tends to prevent coprecipitation of other metals.

The purpose of this research was to study the effect of metal-metal bonding on the properties of complexes in which they exist. The -Ni-Ni- and -Pd-Pd- bond lengths in several complexes have been measured and compared with

a) the relative strengths of the metal-metal bonds as determined by measurement of the absorption spectra of single crystals using plane polarized light, b) the solubilities in chloroform and in 1,2-dichlorobenzene, c) the molar solubilities and solubility products in water, and d) the color of the solid complex.

It is hoped that the results of this work will give a more thorough understanding of the selectivity of vic-dioximes as analytical reagents for nickel and palladium, and might aid in the future design and improvement of analytical reagents for other metals.

B. Nomenclature and Notation

In this thesis the vic-dioximes and their complexes will, in general, be called by their trivial names. In order to avoid any possible confusion the structures, systematic names, and trivial names of most of the compounds used in this work are listed in Table 1. Any compounds not listed will be similar enough to those in the table that their structure will be apparent.

The systematic naming of complex compounds is based on the general rules set forth by Fernelius and his coworkers (30, 31). The systematic names of the vic-dioximes are those proposed by the International Union of Chemistry (64).

Table 1. Structures and nomenclature of compounds used in this research

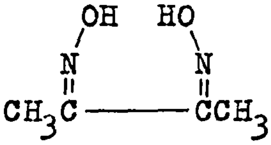
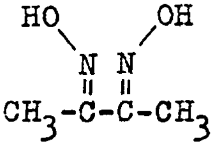
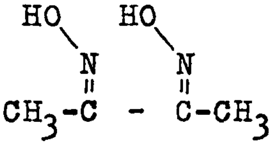
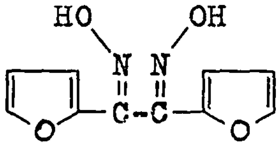
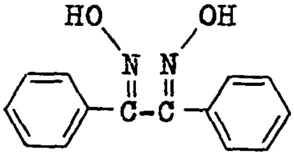
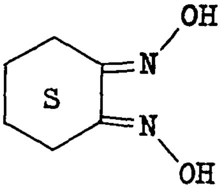
Structure	Systematic name Trivial name
	*syn*-2,3-butanedionedioxime *syn*-dimethylglyoxime
	*anti*-2,3-butanedionedioxime *anti*-dimethyglyoxime
	*amphi*-2,3-butanedionedioxime *amphi*-dimethylglyoxime
	1,2-di(2-furyl)ethanedione-dioxime α-furildioxime
	1,2-diphenylethanedionedioxime α-benzildioxime
	1,2-cyclohexanedionedioxime nioxime

Table 1. (Continued)

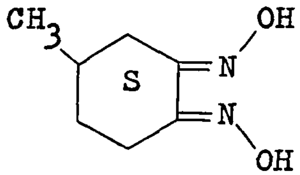
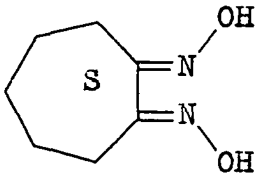
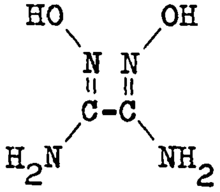
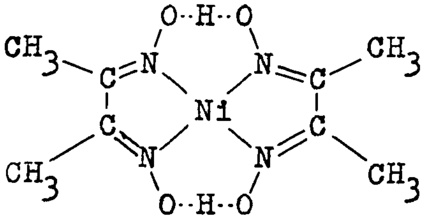
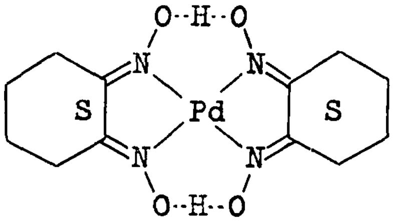
Structure	Systematic name Trivial name
	4-methyl-1,2-cyclohexanedionedioxime 4-methylnioxime
	1,2-cycloheptanedionedioxime heptoxime
	1,2-diaminoethanedionedioxime diaminoglyoxime
	bis(2,3-butanedionedioximato-*N*,*N*') nickel(II) nickel dimethylglyoxime
	bis(1,2-cyclohexanedione-dioximato-*N*,*N*') palladium(II) palladium nioxime

Table 2. Notation used in this thesis

Symbol	Meaning of Symbol
A	Absorbancy or a constant in the Debye-Hückel equation.
A.U.	Angstrom units.
a_i	Activity of species *i*.
B	A constant in the second approximation of the Debye-Hückel equation.
c_i	Molar concentration of species *i*.
d	Distance between planes in a crystal in Angstrom units.
d'	Apparent distance between planes in a crystal in Angstrom units.
DH_2	Represents a *vic*-dioxime.
DH^-	The anion of a *vic*-dioxime.
f_i	The activity coefficient of species *i*.
K_{DH_2}	The first acid dissociation constant of a *vic*-dioxime.
K_{sp}	Solubility product.
l	Length of the light path through a solution.
M^{++}	A divalent metal ion.
m_i	The total amount of an atom or molecule in a solution, irregardless of the particular species in which it exists, expressed in moles per liter.
mu	Wavelength of light expressed in millimicrons.
R	Radius of x-ray diffraction camera.
s	Length of the arc between two spots on an x-ray diffraction photograph.
S	Solubility expressed in moles per liter.

Table 2. (Continued)

Symbol	Meaning of Symbol
t	Thickness of crystal in absorption measurements.
a_i	Effective ionic diameter in the second approximation to the Debye-Hückel equation.
β	The half width of an electronic absorption band.
ϵ	Molar absorptivity.
λ	Wavelength of light.
τ	Time of exposure of photographic plate in the measurement of absorption spectra of crystals.
μ	Ionic strength.
θ	The angle of x diffraction in the Bragg equation.
$\perp$	Means that the plane of polarized light is perpendicular to the plane of the molecule in a crystal.
$\parallel$	Means that the plane of polarized light is parallel to the plane of the molecules in a crystal.

As will be seen later, only the anti isomer of a vic-dioxime is capable of forming the characteristic 2:1 complex with nickel, palladium, and platinum. Therefore, when discussing the vic-dioximes and their metal complexes it will be understood that the dioxime is of the anti configuration. In cases where the configuration is different these will be indicated.

In most cases the notation used will be obvious. Again, in order to avoid any possible confusion the symbols used in this thesis are listed and explained in Table 2.

The symbols and nomenclature used in connection with absorption spectrophotometry are in accordance with the recommendations of Hughes *et al*. (46) and of Gibson (34).

II. REVIEW OF THE LITERATURE

A. Constitution of vic-Dioxime Complexes

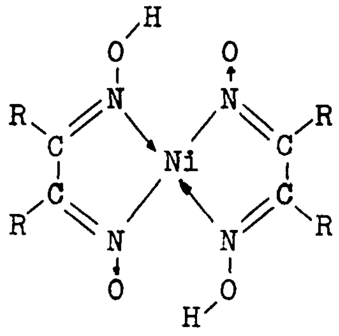
In 1905 L. Tschugaeff (82) showed that nickel(II), palladium(II), and platinum(II) react with vic-dioximes according to the equation

$$M^{++} + 2\ DH_2 = M(DH)_2 + 2\ H^+ ,$$

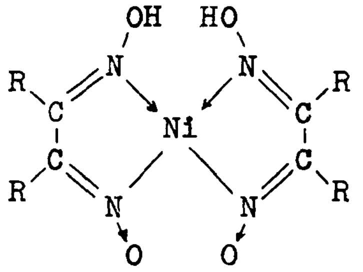
thus showing that the ratio of dioxime to metal is 2:1, and that two moles of hydrogen are liberated in the reaction. Of the three stereoisomers of a vic-dioxime, the syn, anti, and amphi, only one was found to give the characteristic 2:1 complex. One isomer forms a relatively unstable 1:1 complex (1, 44, 59) and the third isomer does not react with metals at all.

For many years the determination of the constitution of the 2:1 complex was hampered by the incorrect assignment of configurations to these isomers. In 1921, Meisenheimer (58) showed that it is the anti isomer rather than the syn isomer that is responsible for the formation of the 2:1 complex.

Pfeiffer and his coworkers (69) showed that coordination occurs through the nitrogen atoms and not through an oxygen. He wrote the structure of the complex as II.

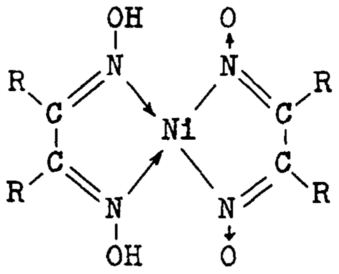


II

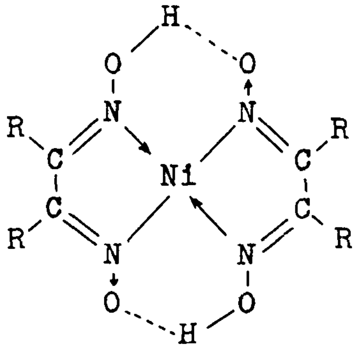


III

Because of their failure to isolate isomers of the types II, III, and IV, Brady and Muers (12) suggested that these structures are either in rapid equilibrium or the hydrogen atoms are involved in hydrogen bonding as in V.



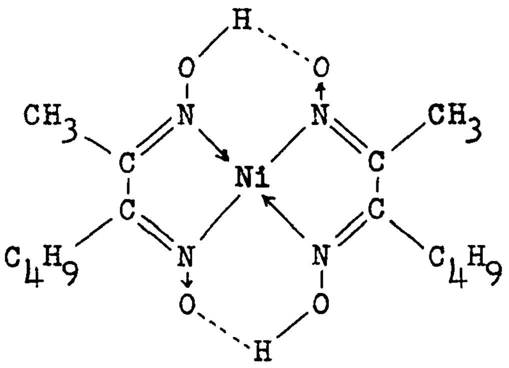
IV



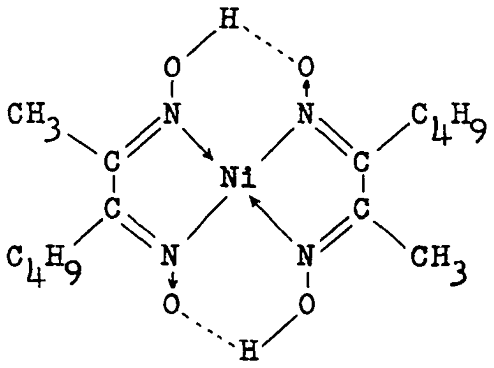
V

They indicated a preference for the hydrogen bonded structure since this would account for the unreactive nature of the -OH groups which they and other workers (85, 7) observed.

Such a hydrogen bonded structure requires a square planar configuration. That this is true has been shown by Sugden (80) and by Cavell and Sugden (20), who prepared cis and trans isomers of nickel methyl-n-butylglyoxime, VI and VII.



VI



VII

In like manner, Dwyer and Mellor (28) showed that the palladium(II) complexes are square planar. Furthermore, several workers (19, 52, 6a) have shown that these complexes are diamagnetic and therefore, according to Pauling (65), contain dsp^2 square planar bonds.

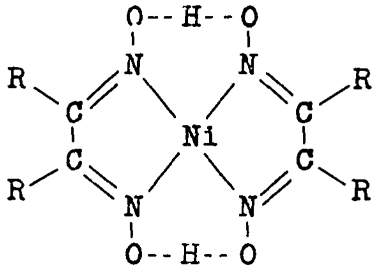
Godycki (37) and Voter (91) and their coworkers studied the infrared absorption spectra of dimethylglyoxime, nioxime, and heptoxime, and the nickel complexes of these compounds. The deuterated complexes were also studied. In the nickel complexes they found no bands due to free or to associated -OH groups in the region in which they usually occur. It was noted that the O--H--O bond distance is unusually short, and in fact, is shorter than any previously reported. Thus, it was concluded that the O--H--O bond is extremely strong and therefore has a greatly displaced and diffuse absorption band. It was further suggested that the hydrogen bond is symmetrical, that is, the hydrogen atom is equally bound to both oxygen atoms.

Rundle and Parasol (76) were able to decide that the very weak diffuse band at 5.63 μ in nickel dimethylglyoxime is due to the O--H--O bonds. They plotted the O--H--O distances for several different compounds known to have hydrogen bonds in which the hydrogen atom lies on the axis between the two oxygen atoms against the frequency at which these bonds absorb. Since the O--H--O distance in nickel dimethylglyoxime was known, this plot indicated the approximate position of the desired band. In the deuterated complex this band disappears.

Evidence for the symmetrical nature of the hydrogen bonds in nickel dimethylglyoxime was also given by Rundle and Parasol (76). Only one N-O absorption band is observed, while if the hydrogen bonds were not symmetrical one should observe two such bands.

Tujita, Nakahara, and Tsuchida (89) studied the hydrogen bonds in dimethylglyoxime complexes of cobalt(III) and concluded that these compounds also contain strong symmetrical hydrogen bonds. Copper dimethylglyoxime has also been shown to contain strong hydrogen bonds which are probably symmetrical (36).

Taking all the evidence into account, one must then write the structure of square planar complexes of vic-dioximes as VIII.



VIII

B. Crystal Structure of vic-Dioxime Complexes and Metal-Metal Bonds

The crystal structure of nickel dimethylglyoxime has been determined by Godycki and Rundle (36). As expected, they found the molecule to be square planar and to have the bond lengths and angles shown in Figure 1. Nickel positions in the crystal are 000, 00 1/2, 1/2 1/2 1/2, and 1/2 1/2 0. The nickel atoms lie in a straight row that extends throughout the length of the crystal, as shown in Figure 2. The distance between two adjacent nickel atoms was found to be 3.24 A.U., which Godycki and Rundle believed to be short enough to allow weak intermolecular nickel-nickel bonds.

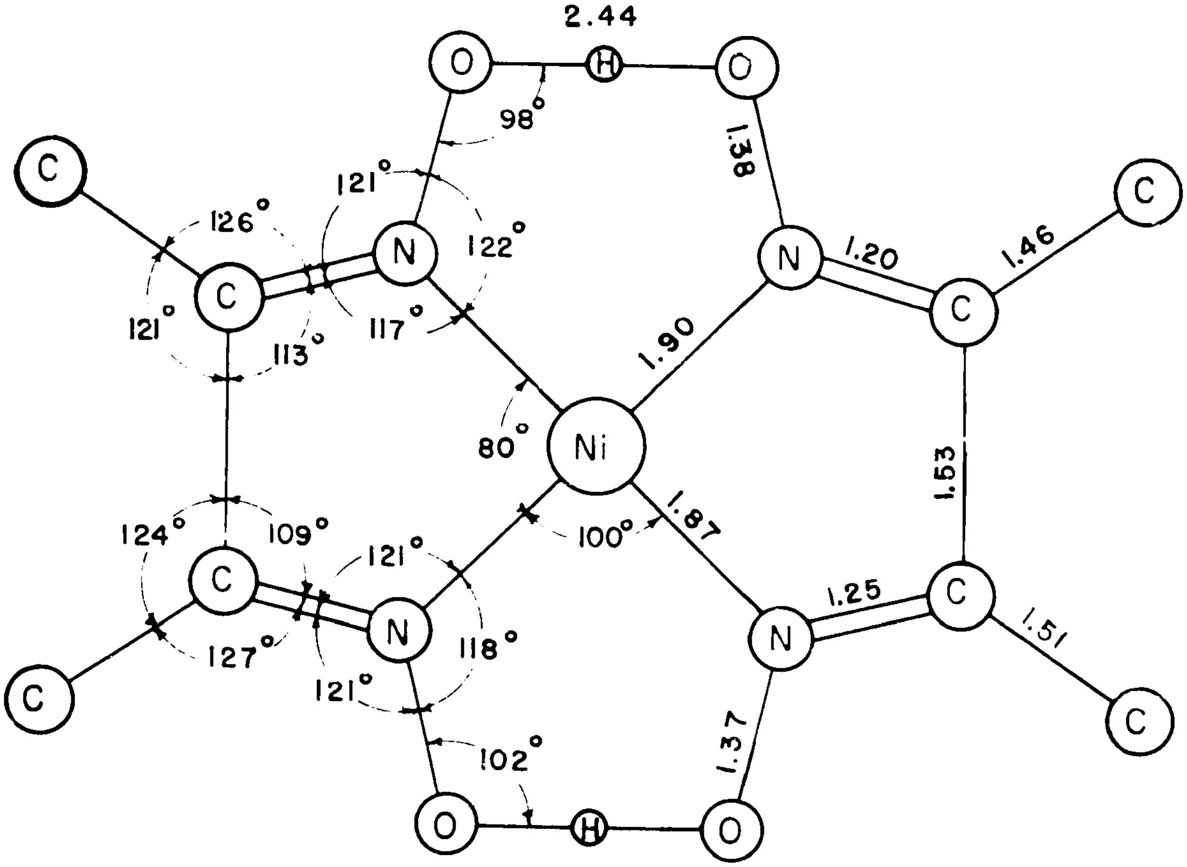

2.44
O
H
O
98°
1.38
C
126°
121°
N
122°
N
1.20
C
1.46
C
C
121°
117°
113°
1.90
80°
Ni
1.53
124°
109°
100°
1.87
121°
C
1.25
C
N
118°
N
127°
1.51
C
121°
C
102°
1.37
O
H
O

Figure 1. Bond lengths and bond angles in nickel dimethylglyoxime

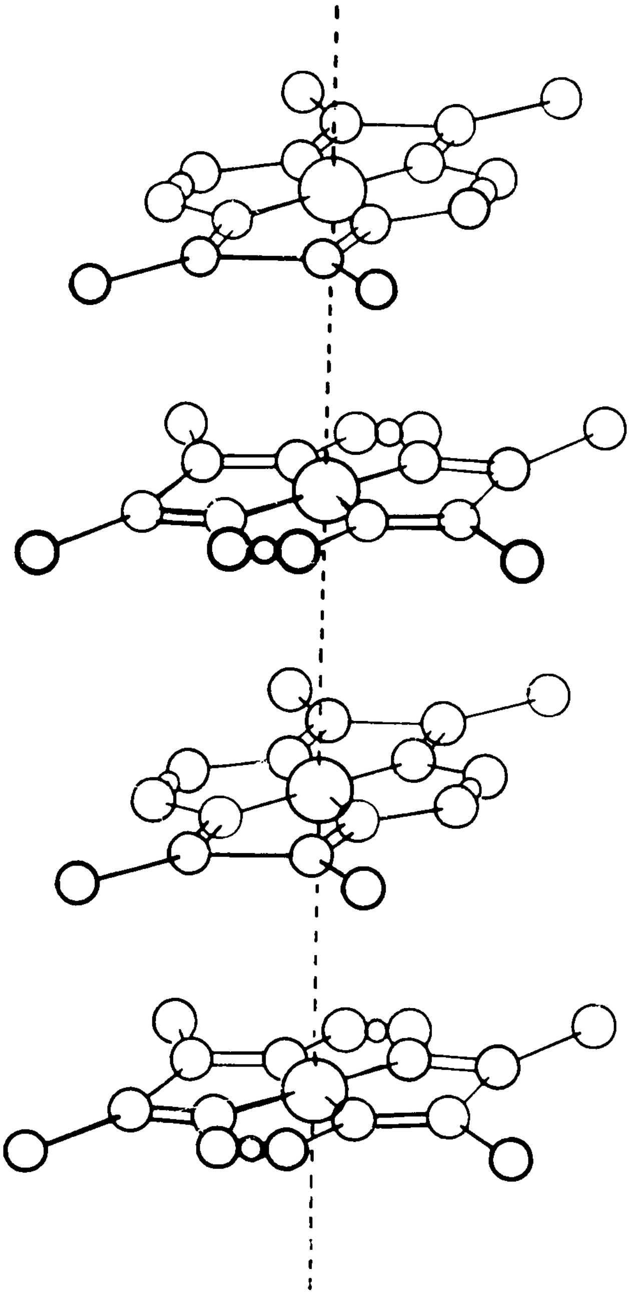


Figure 2. Crystal structure of nickel dimethylglyoxime

Previous to the present work several metal complexes of _vic_-dioximes have been shown to have the same crystal structure as nickel dimethyglyoxime. These are listed below in Table 3.

Table 3. Metal-metal bond lengths in some complexes of _vic_-dioximes having the same crystal structure as nickel dimethylglyoxime

Complex	-M-M- distance	Reference
nickel dimethylglyoxime	3.24	(36,66,79)
nickel nioxime	3.24	(36)
nickel methylethylglyoxime	3.4	(79)
palladium dimethylglyoxime	3.25	(36,66,79)
palladium methylethylglyoxime	3.4	(79)
platinum dimethylglyoxime	3.25	(66,79)
platinum methylethylglyoxime	3.4	(79)

In this work this list of complexes has been expanded considerably.

These compounds crystallize in the form of long thin needles in which the ratio of length to width is about 100:1. The metal-metal bonds are parallel to the needle, or _c_ axis, and the plane of each molecule is perpendicular to this axis.

Bua and his coworkers (16, 17, 78) have determined the structure of copper dimethylglyoxime. This complex has the same molecular structure as of nickel dimethylglyoxime, however, it packs differently in the crystal so that no chains of -Cu-Cu- bonds are possible.

Godycki and Rundle (36) cited the difference in dichroism between the nickel and copper complexes as evidence for the presence of chains of -Ni-Ni- bonds. Yamade and Tsuchida (96) using plane polarized light measured the absorption spectra of microscopic crystals of these two complexes. For copper dimethylglyoxime and other "normal" square planar complexes, maximum absorption occurs when the plane of polarized light is parallel to the plane of the molecules. However, for the nickel(II) and platinum(II) complexes of dimethylglyoxime, they found that maximum absorption occurs when the plane of polarized light is perpendicular to the plane of the molecules, that is, parallel to the metal-metal bonds. They interpreted this to indicate an interaction between adjacent nickel atoms.

In the same manner, Yamada (95) has shown that a similar interaction exists between platinum atoms in crystals of the Magnus green salt, $\left[Pt(NH_3)_4\right]\left[PtCl_4\right]$, and also in the salt $\left[Pt(NH_3)_4\right]\left[PtBr_4\right]$. Each of these salts also exists in another modification which is pink. The pink salts as well as such salts as $Pt(NH_3)_4Cl_2$ and K_2PtCl_4 show maximum absorption in the visible region when the plane of polarized light is parallel to the plane of the molecules. The green isomers however, show the opposite behavior. The crystal structures of the two modifications of $\left[Pt(NH_3)\right]\left[PtCl_4\right]$ have been studied by Cox, et al. (23) and by Atoji, Richardson, and Rundle (2). The latter group has proposed that the green salt contains chains of -Pt-Pt- bonds, 3.25 A.U. in length, which give rise to the unusual color and dichroism. Cox and his coworkers (23) also commented on the unusual dichroism and packing in the crystal. It should be noted that the -Pt-Pt- bond length here agrees closely with the -Ni-Ni- bond length in nickel dimethylglyoxime.

Rundle (73) has also shown that similar -Au-Au- bonds, 3.26 A.U. in length, exist in the gold(III) complex of dimethylglyoxime, $\left[Au^{III}(DH)_2\right]\left[Au^{I}Cl_2\right]$. The chains consist of alternate Au(III) and Au(I) atoms.

The nature of the bonding in metal chains has been discussed by Godycki and Rundle (36) and by Rundle (74, 75). In valence bond terms, the bonding can be thought of as due to the partial promotion of a non-bonding 3d-electron to the 4p shell, thus giving a small amount of octahedral d^2sp^3 character to each nickel atom.

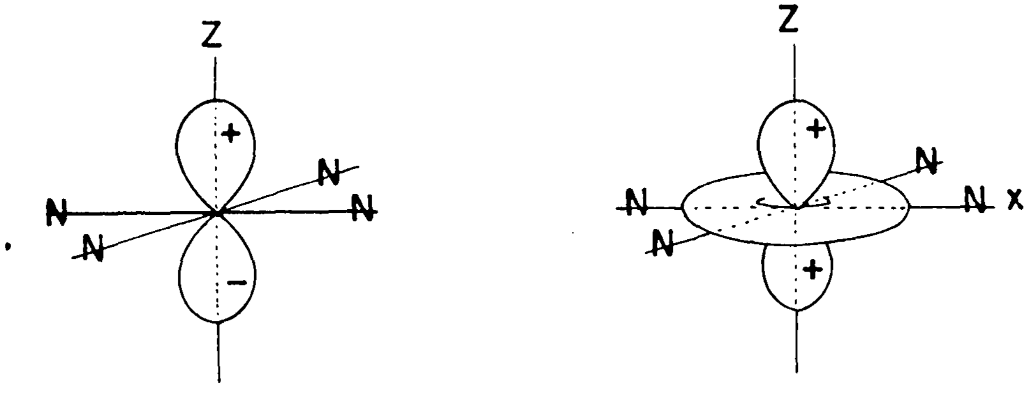
Rundle believes that the molecular orbital description is more appropriate for metal-metal bonding.

In nickel dimethylglyoxime, for example, the dsp^2 square planar bonds lie in the xy plane. Extending along the z axis, above and below the plane of the molecule is the $3d_{z^2}$-orbital, which contains two non-bonding electrons, and the $4p_z$-orbital, which is empty. These orbitals are illustrated in Figure 3.

First, consider the formation of a dimer in which two molecules of nickel dimethylglyoxime approach along their z axes and form a Ni-Ni bond. The two $3d_{z^2}$-orbitals combine to form an a_{1g} bonding orbital and an a^*_{1u} anti-bonding orbital. Similarly, the two $4p_z$-orbitals combine to form an a_{1g} bonding orbital and an a^*_{1u} anti-bonding orbital. This is illustrated schematically in Figure 3. The four electrons will then be in the a_{1g} and the a^*_{1u} molecular orbitals, but since one of these orbitals is bonding and the other is anti-bonding, there is no net decrease in energy and therefore, no bonding. However, in order to decrease electron repulsion, electrons may be partially promoted from the a^*_{1u} to the empty a_{1g} orbital. This process is enhanced somewhat because it results in weak Ni-Ni bonds. The phenomenon is called "configuration interaction".

C. The Selectivity of vic-Dioximes as Analytical Reagents for Nickel and Palladium

The presence of strong symmetrical hydrogen bonds undoubtedly contributes to the stability of vic-dioxime complexes. The fact that the selectivity of vic-dioximes for nickel and palladium is not due to their unusually high stability has been established by Charles and Freiser (21), who measured the equilibrium constants, ΔH, and ΔS for the


Z
+
N
N
N
N
−
Z
+
N
N
N
x
N
+

a $4p_z$ − ORBITAL a $3d_{z^2}$ − ORBITAL

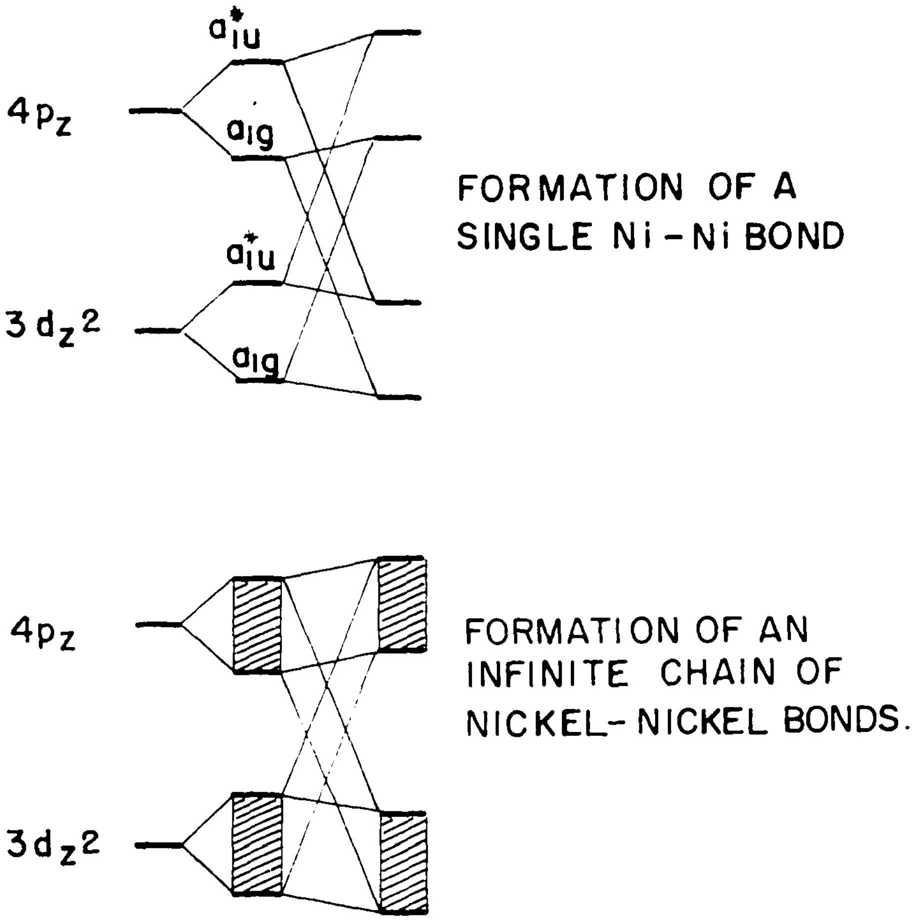

a^*_{1u}
$4p_z$
a_{1g}
a^*_{1u}
$3d_{z^2}$
a_{1g}
FORMATION OF A SINGLE Ni - Ni BOND
$4p_z$
$3d_{z^2}$
FORMATION OF AN INFINITE CHAIN OF NICKEL- NICKEL BONDS.

Figure 3. Atomic orbitals involved in nickel-nickel bonding and schematic illustration of the formation of nickel-nickel bonds

reaction

$$M^{++}(aq.) + 2\ DH^{-}(aq.) = Ni(DH)_2(aq.)$$

in 50% dioxane-water. The metal was copper(II) and nickel(II), and the vic-dioxime was dimethylglyoxime and its O-methyl ether. Hydrogen bonding is not possible in the O-methyl ether complex. They found that for both ligands the copper(II) complexes are more stable than the nickel(II) complexes. Since this is just the usual order of stability of chelates found by Irving and Williams (47), the selectivity of dimethylglyoxime must be due to some other factor.

Godycki and Rundle (36) proposed that the reason for the selectivity of dimethylglyoxime is that the metal-metal bonds contribute enough stability to the solid nickel complex that it is insoluble. The copper complex, which has the same molecular structure, is soluble, but packs in its crystal in such a way that no such -Cu-Cu- bonds are formed. On the basis of the difference in solubility between nickel dimethylglyoxime and copper dimethylglyoxime, Rundle (73) has calculated that the -Ni-Ni- bonds contribute about 10 kcal./mole to the stability of the nickel complex.

If the metal-metal bonding is responsible for the insolubility of nickel dimethylglyoxime, one might expect to observe an increase in solubility in a series of complexes with longer and longer metal-metal bonds. The longer bonds, which would result from increasing the bulkiness of the *vic*-dioxime, would be expected to become weaker as the bond length became longer and therefore contribute less to the stability of the crystal. With this view in mind, Hooker (6a,45) prepared a series of nickel complexes of substituted nioximes in which the bulkiness of the substituent was taken as a rough measure of the relative lengths of the -Ni-Ni- bonds. Although the results of his work were inconclusive there was some indication that the solubility in chloroform and the color may depend on the metal-metal bonding.

While this work was in progress Sharpe and Wakefield (79) published a paper providing further support for the proposal of Godycki and Rundle (36) that the selectivity of *vic*-dioximes for nickel(II) and palladium(II) is due to chains of metal atoms. These workers prepared the nickel, palladium and platinum complexes of methylethylglyoxime, measured the metal-metal bond lengths, and compared these with the solubilities in water. They also compared the solubilities of nickel nioxime and of the nickel, palladium, and platinum complexes of dimethylglyoxime, for which the metal-metal bond lengths were known from the work of Godycki and Rundle (36). Sharpe and Wakefield concluded that the solubility of these complexes increases as the metal-metal bond length increases, a conclusion which the present work shows must be modified. The reason for this erroneous conclusion is believed to be that the metal-metal bond lengths were not sufficiently accurate, and, as will be shown later, molar solubilities in water can be misleading since they depend on the pH.

III. EXPERIMENTAL

A. Materials

1. vic-Dioximes

"Baker's Analyzed" dimethylglyoxime was recrystallized twice from water.

α-Benzildioxime was obtained from Eastman Organic Chemicals. The "white label" product was recrystallized twice from ethanol.

Nioxime, heptoxime, and α-furildioxime were prepared by other workers in this laboratory. Each one was recrystallized at least three times before use. Nioxime was prepared using the procedures of Rauh, et al. (71), Geissman and Schlatter (33), and of Hach, Banks, and Diehl (38). Heptoxime was prepared by the method of Vander Haar, Voter, and Banks (90), and α-furildioxime by the method of Reed, Banks and Diehl (72).

3-Methylnioxime, 4-methylnioxime, 4-isopropylnioxime, and 4-tert-amylnioxime were prepared in this laboratory by J. Richard and D. Hooker. The procedures used are described by Banks, Hooker, and Richard (6a).

Diaminoglyoxime was prepared in this laboratory by J. LaPlante using the method of Fischer (32). The crude product was recrystallized twice from water.

2. Nickel and palladium complexes of vic-dioximes

Some of the nickel and palladium complexes used in this work were prepared by other workers in this laboratory. They had been recrystallized slowly from organic solvents and were used for x-ray diffraction measurements, determination of absorption spectra, and determination of molar absorptivities without further purification.

Nickel nioxime, nickel heptoxime, palladium nioxime, and palladium heptoxime were prepared in the following manner: Five grams of the recrystallized dioxime was weighed out and dissolved in 95% ethanol. Water was then added and if the dioxime began to precipitate more ethanol was added. In this way the solution was diluted to about 250 ml. A 10% excess of nickel chloride was slowly added in the form of a 1 M solution of "Baker's Analyzed" special low cobalt reagent. In the cases of the two nickel complexes a few drops of 2 M ammonium hydroxide was added. The resulting precipitate was allowed to stand overnight and then washed and separated six times by centrifugation. The precipitate was removed by filtering through a sintered glass crucible, washed once more, and dried for one hour at 110°C.

Palladium nioxime and palladium heptoxime were recrystallized from 1,2-dichlorobenzene (Eastman "white lable" 99 + %). Nickel heptoxime was found to form the largest crystals from trichloroethylene (Baker, purified), and nickel nioxime from nitrobenzene (Fisher "Certified" reagent).

In each case, a solution of the complex was prepared that was saturated at about 90°C. This solution was filtered, while hot, into a clean 50-ml. or 100-ml. volumetric flask. The solution was then warmed up to about 90° again and placed in a Dewar flask which had just been filled with boiling water. The volumetric flask was stoppered tightly and suspended in the Dewar flask from a wire so that only the top of the volumetric flask was above the water level. The Dewar flask was stoppered and set aside for 24 hours to cool. In this way fairly large crystals could be obtained. They were separated by filtering through filter paper, the excess solvent quickly washed away with ether, and dried in the air.

B. Apparatus

1. Spectrophotometers

For the measurement of absorption spectra of solutions, colloidal suspensions, and powders pressed into KBr discs, a Cary Model 14 recoding spectrophotometer was used, manufactured by the Applied Physics Corporation. Molar absorptivities and other measurements of absorbancy at a particular wavelength were made with a Beckman DU spectrophotometer equiped with a photomultiplier attachment.

C. Measurement of Metal-Metal Bond Lengths

Metal-metal bond lengths were measured by means of x-ray diffraction. For complexes of which single crystals could be obtained, the back reflection Weissenberg was used. This method permits measurement of lattice constants to about ± 0.005 A.U. or better. When single crystals could not be obtained the metal-metal bond length was measured from an x-ray powder photograph. The accuracy of the powder technique is believed to be about ± 0.03 A.U.

1. Back reflection technique using single crystals

The crystal is placed in the path of an x-ray beam in the center of a cylindrical camera, and a piece of photographic film is wrapped around the inside of the cylinder to record the diffraction pattern. A synchronous motor drives a mechanism that oscillates the crystal through a 180° arc and at the same time the camera moves back and forth along the axis of the cylinder. This arrangement is shown schematically in Figure 4, and the type of diffraction pattern obtained is shown in Figure 5. The crystal was rotated about either the a or b axis.

Unfiltered radiation was used in order to obtain as many reflections as possible. An x-ray tube with a copper target was used, giving radiation of the following wavelengths:

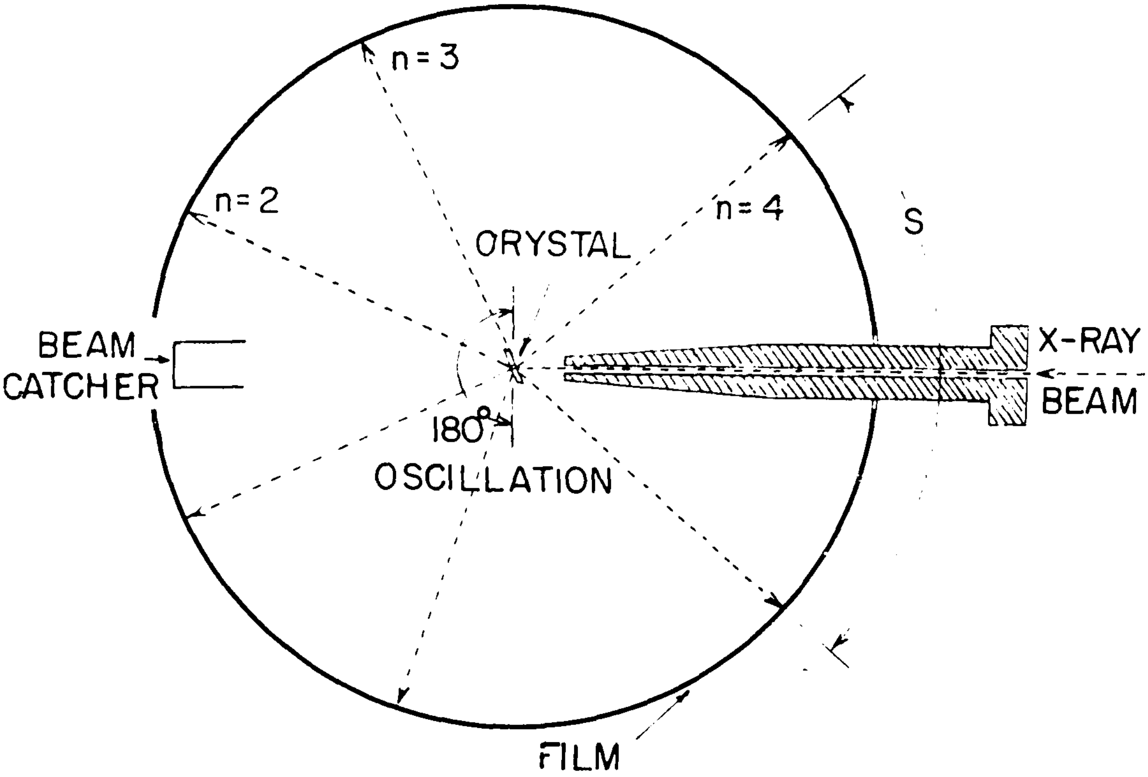
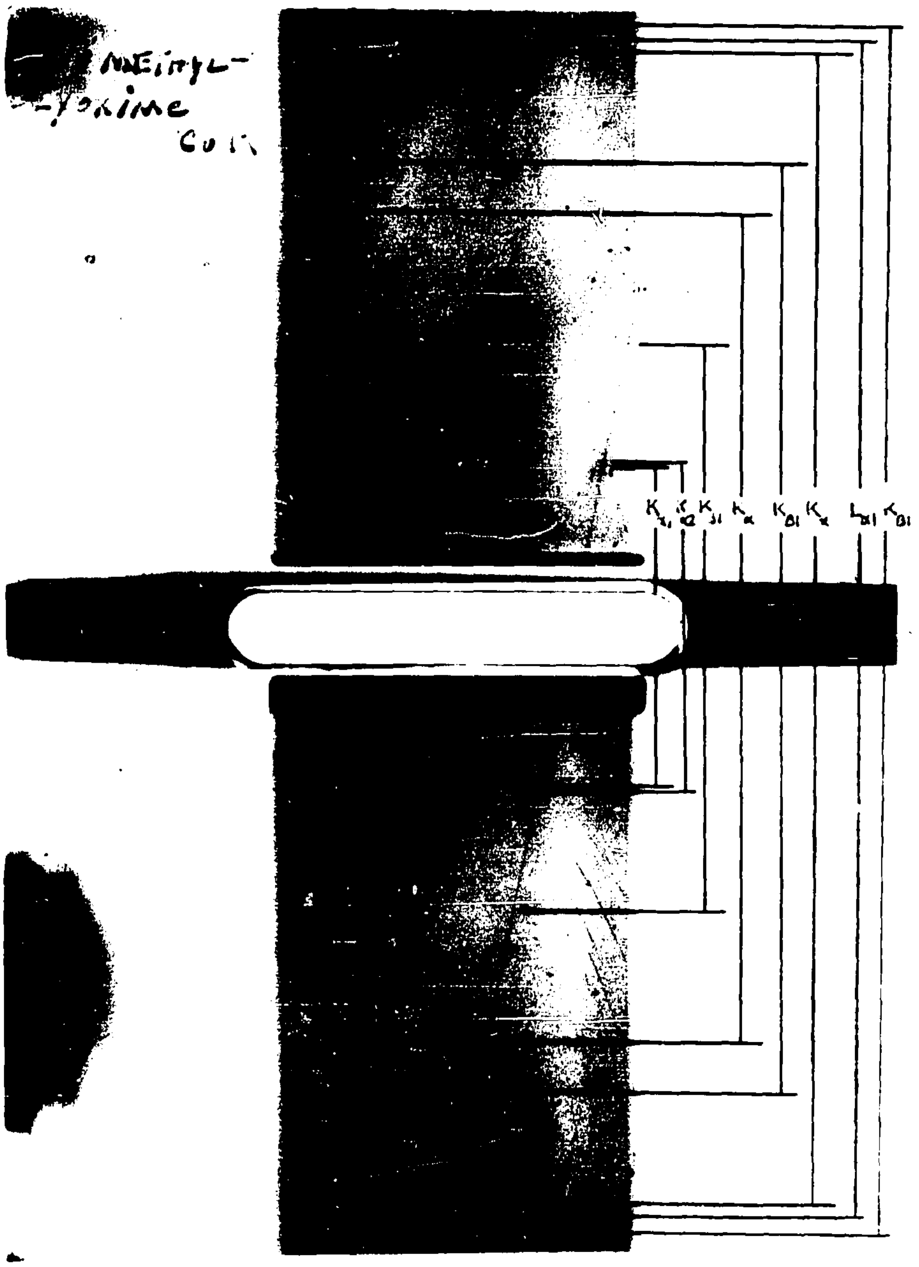

n = 3
n = 2
n = 4
S
CRYSTAL
BEAM CATCHER
X-RAY BEAM
180°
OSCILLATION
FILM

Figure 4. Schematic diagram of back reflection camera

Figure 5. Typical back reflection diffraction pattern of a crystal with the nickel dimethylglyoxime structure, showing the arcs from which the metal-metal bond length is calculated


Methyl-
-yoxime
Cu K
$K_{\alpha 1}$
$K_{\alpha 2}$
$K_{\beta 1}$
K_{α}
$K_{\beta 1}$
K_{α}
$L_{\alpha 1}$
$K_{\beta 1}$

$K_{\alpha 1}$ = 1.54050 A.U.

$K_{\alpha 2}$ = 1.54434 A.U.

$K_{\beta 1}$ = 1.39217 A.U.

$L_{\alpha 1}$ = 1.47636 A.U.

$K_{ave.}$ = 1.5418 A.U.

The $L_{\alpha 1}$ radiation is from tungsten impurities in the target. The wavelengths of $K_{\alpha 1}$ and $K_{\alpha 2}$ radiation are so close together that in the front reflection region these two spots overlap. One then uses a weighted average, $K_{ave.}$, for the wavelength.

It was necessary to make four day exposures in order to see the higher order reflections. In each case reflections were obtained for n = 2, 3, and 4.

After the film was developed and dried it was laid out flat and the length of the arc, s, in Figures 4 and 5 measured accurately for each reflection. The value of θ was then calculated from the equation

$$\theta \text{ (in radians)} = \frac{\pi}{2} - \frac{s}{4R}, \qquad (3.1)$$

where R, the radius of the camera, is 3.581 cm. For each reflection an apparent value of the metal-metal distance, d', was calculated from the Bragg equation:

$$d' = \frac{n\lambda}{2 \sin \theta} \qquad (3.2)$$

Certain systematic errors are eliminated from these values of the metal-metal bond length by extrapolating to a value of sin $\theta = 1$, that is, the point at which the x-ray beam is reflected directly back upon itself. The type of extrapolation used depends on which error is the most predominant. If the predominant error is due to film shrinkage during development, one plots the apparent metal-metal bond length against $(\pi/2 - \theta) \cot \theta$. If the predominant error is due to absorption of the x-rays by the crystal one plots against $\cot \theta \cos^2 \theta$. If failure to have the crystal exactly in the center of the camera is the main source of error, then one plots against $\cos^2 \theta$. Extrapolations using these three functions of θ are compared in Figure 6. The same functions were tried with two other crystals, and it was found that in each case the function $\cot \theta \cos^2 \theta$ came the closest to giving a straight line. It was therefore used in all subsequent extrapolations. The extrapolations actually used are shown in Figures 7 and 8, and the data for these are reported in Tables 4 through 13.

The back reflection method for measuring lattice constants is discussed in detail by Buerger (18).

Figure 6. Comparison of different extrapolation methods for determining metal-metal bond lengths

Curve 1, $f(\theta) = \cos^2 \theta$;

Curve 2, $f(\theta) = (\pi/2 - \theta) \cot \theta$;

Curve 3, $f(\theta) = \cot \theta \cos^2 \theta$.

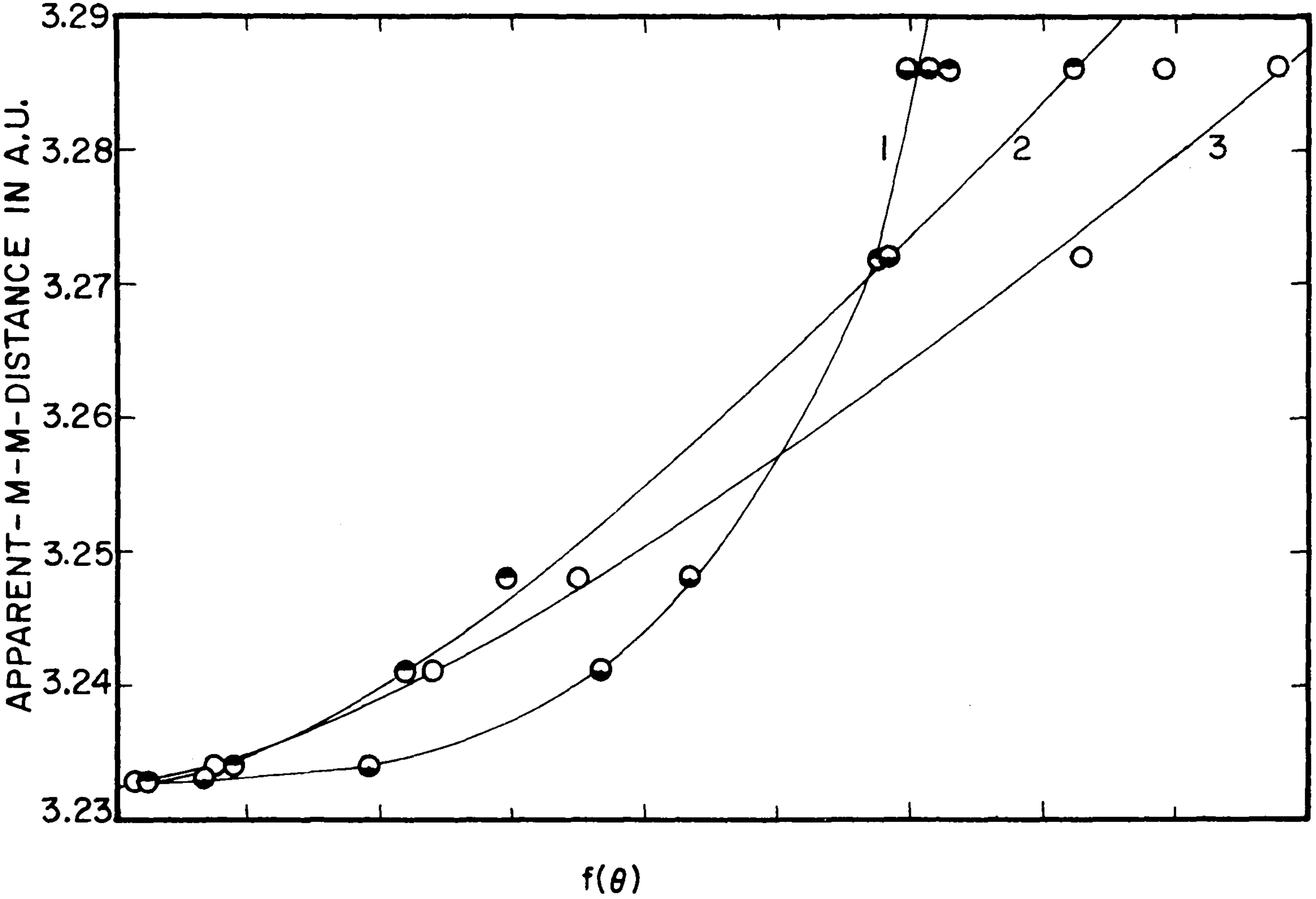


Figure 6. Comparison of different extrapolation methods for determining metal-metal bond lengths

Figure 7. Extrapolation of nickel-nickel bond lengths to the back reflection point

Curve 1, nickel dimethylglyoxime;

Curve 2, nickel nioxime;

Curve 3, nickel α-furildioxime;

Curve 4, nickel α-benzildioxime;

Curve 5, nickel heptoxime.

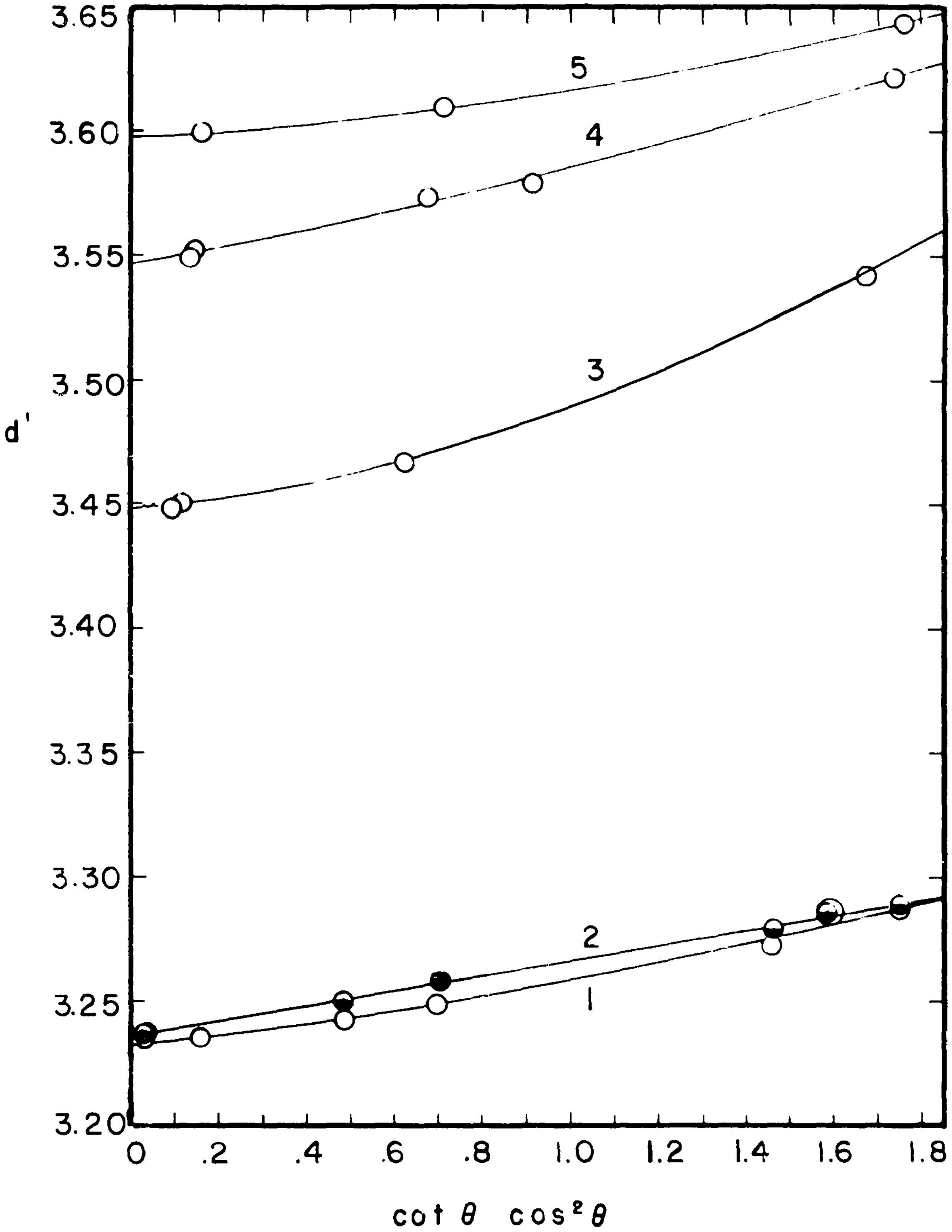

3.65
3.60
3.55
3.50
3.45
3.40
3.35
3.30
3.25
3.20
d'
0
.2
.4
.6
.8
1.0
1.2
1.4
1.6
1.8
cot θ cos²θ
5
4
3
2
1

Figure 8. Extrapolation of palladium-palladium bond lengths to the back reflection point

Curve 1, palladium nioxime;

Curve 2, palladium dimethylglyoxime;

Curve 3, palladium heptoxime;

Curve 4, palladium α-furildioxime;

Curve 5, palladium α-benzildioxime.

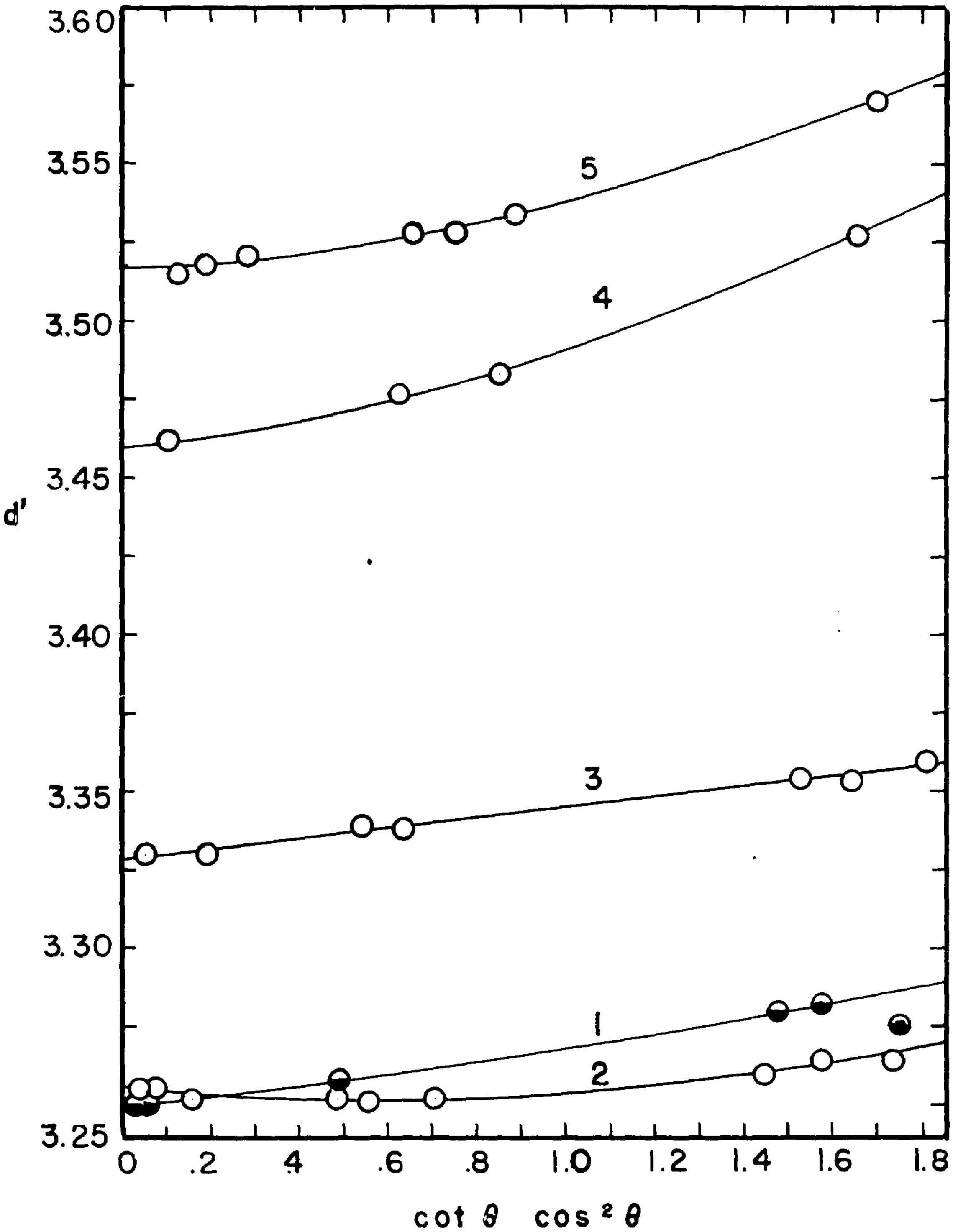

3.60
3.55
3.50
3.45
3.40
3.35
3.30
3.25
d'
5
4
3
1
2
0
.2
.4
.6
.8
1.0
1.2
1.4
1.6
1.8
cot θ cos² θ

Table 4. Measurement of the nickel-nickel bond length in nickel dimethylglyoxime

n	λ	s	θ	$\cot\theta\cos^2\theta$	d'
4	1.5405	4.42	72°20'	0.029	3.233
4	1.5443	4.30	72°49'	0.027	3.233
4	1.3922	7.65	59°25'	0.153	3.234
3	1.5418	11.12	45°32'	0.482	3.241
3	1.3922	12.50	40°01'	0.699	3.248
2	1.5418	15.47	28°07'	1.456	3.272
2	1.4764	15.83	26°42'	1.587	3.286
2	1.3922	16.24	25°04'	1.754	3.286

Table 5. Measurement of the nickel-nickel bond length in nickel nioxime

n	λ	s	θ	$\cot\theta\cos^2\theta$	d'
4	1.5443	4.36	72°34'	0.028	3.237
4	1.5405	4.46	72°10'	0.030	3.237
3	1.5418	11.16	45°22'	0.487	3.250
3	1.3922	12.53	39°51'	0.706	3.259
2	1.5418	15.49	28°03'	1.462	3.279
2	1.4764	15.83	26°42'	1.587	3.286
2	1.3922	16.24	25°03'	1.756	3.288

Table 6. Measurement of the nickel-nickel bond length in nickel α-furildioxime

n	λ	s	θ	$\cot\theta\cos^2\theta$	d'
4	1.5443	6.604	63°35'	0.0983	3.449
4	1.5405	6.692	63°14'	0.1023	3.450
3	1.5418	12.040	41°50'	0.6202	3.468
2	1.5418	16.051	25°48'	1.677	3.542

Table 7. Measurement of the nickel-nickel bond length in nickel α-benzildioxime

n	λ	s	θ	$\cot\theta\cos^2\theta$	d'
4	1.5443	7.38	60°30'	0.137	3.549
4	1.5405	7.46	60°09'	0.142	3.552
3	1.5418	12.41	40°21'	0.684	3.572
3	1.3922	13.58	35°42'	0.918	3.579
2	1.5418	16.20	25°12'	1.740	3.621

Table 8. Measurement of the nickel-nickel bond length in nickel heptoxime

n	λ	s	θ	$\cot\theta\cos^2\theta$	d'
4	1.5418	7.747	59°00'	0.159	3.598
3	1.5418	12.539	39°50'	0.707	3.609
2	1.5418	16.243	25°02'	1.758	3.644

Table 9. Measurement of the palladium-palladium bond length in palladium dimethylglyoxime

n	λ	s	θ	$\cot\theta\cos^2\theta$	d'
4	1.5443	4.585	71°40'	0.033	3.254
4	1.5405	4.705	71°11'	0.035	3.255
4	1.4764	6.220	65°07'	0.082	3.255
4	1.3922	7.775	58°53'	0.161	3.252
3	1.5418	11.165	45°20'	0.489	3.253
3	1.4764	11.770	42°56'	0.576	3.251
3	1.3922	12.515	39°57'	0.702	3.252
2	1.5418	15.440	28°14'	1.446	3.260
2	1.4764	15.780	26°53'	1.569	3.264
2	1.3922	16.190	25°15'	1.734	3.264

Table 10. Measurement of the palladium-palladium bond length in palladium nioxime

n	λ	s	θ	$\cot\theta\cos^2\theta$	d'
4	1.5443	4.535	71°51'	0.032	3.250
4	1.5405	4.655	71°23'	0.034	3.251
3	1.5418	11.195	45°13'	0.492	3.258
2	1.5418	15.490	28°02'	1.463	3.280
2	1.4764	15.815	26°44'	1.584	3.282
2	1.3922	16.210	25°09'	1.745	3.276

Table 11. Measurement of the palladium-palladium bond length in palladium α-furildioxime

n	λ	s	θ	$\cot\theta\cos^2\theta$	d'
4	1.5443	6.720	63°07'	0.104	3.462
4	1.5405	6.775	62°54'	0.106	3.461
3	1.5418	12.075	41°41'	0.623	3.477
3	1.3922	13.290	36°50'	0.855	3.483
2	1.5418	16.020	25°55'	1.664	3.528

Table 12. Measurement of the palladium-palladium bond length in palladium α-benzildioxime

n	λ	s	θ	$\cot\theta\cos^2\theta$	d'
4	1.5443	7.130	61°29'	0.124	3.515
4	1.5405	7.220	61°07'	0.129	3.519
4	1.3922	9.430	52°16'	0.290	3.521
3	1.5418	12.260	40°57'	0.657	3.529
3	1.4764	12.775	38°53'	0.751	3.528
3	1.3922	13.445	36°13'	0.889	3.534
2	1.5418	16.100	25°35'	1.699	3.570

Table 13. Measurement of the palladium-palladium bond length in palladium heptoxime

n	λ	s	θ	$\cot\theta\cos^2\theta$	d'
4	1.5443	5.485	68°04'	0.056	3.330
4	1.5405	5.580	67°41'	0.059	3.330
4	1.3922	8.325	56°43'	0.198	3.330
3	1.5418	11.535	43°50'	0.542	3.339
3	1.4764	12.110	41°33'	0.632	3.338
2	1.5418	15.655	27°22'	1.524	3.354
2	1.4764	15.965	26°08'	1.643	3.352
2	1.3922	16.380	24°29'	1.819	3.360

2. Powder technique

Suitable crystals of the nickel complexes of the substituted nioximes could not be obtained. It was noticed that the crystals of nickel nioxime were much smaller than those of other complexes, and the formation of large crystals of substituted nioxime complexes is probably further hampered by the large number of cis trans isomers which are possible. It was necessary to measure the nickel-nickel distance in these crystals from powder photographs.

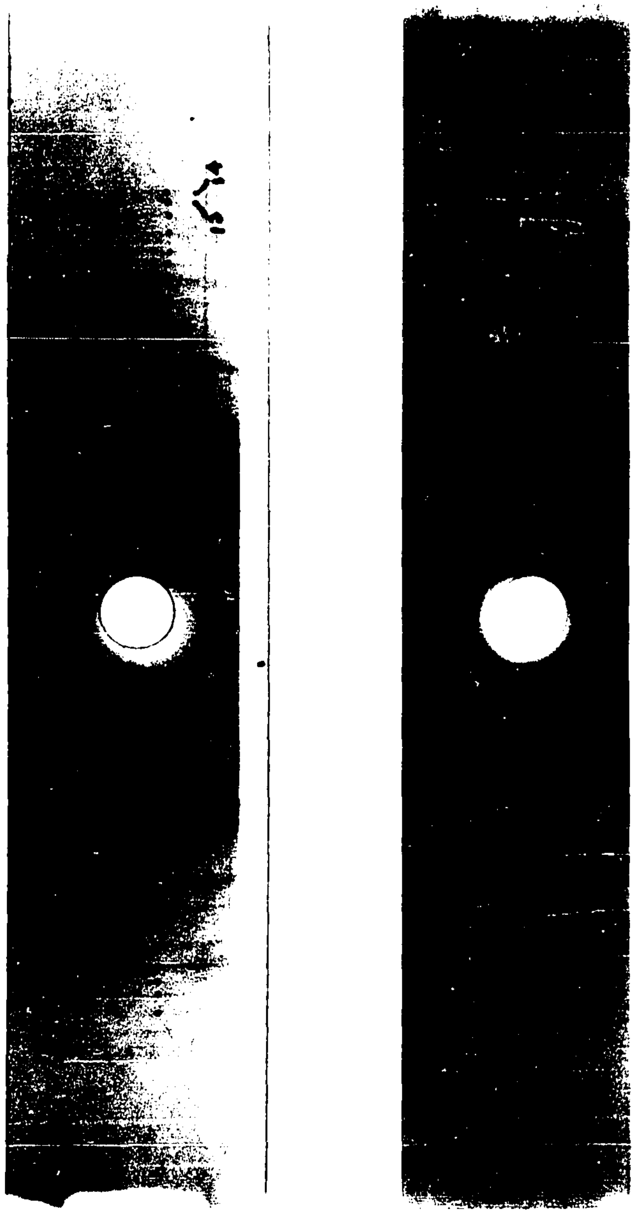
X-radiation from a copper target was passed through a nickel filter so that only the K_α lines would appear on the photograph.

In order to calculate the metal-metal bond length it was first necessary to determine which lines are the (001) reflections. Each line is subject to the condition that $h + k + l = 2n$ (36), and

$$\frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2} = \frac{4 \sin^2 \theta}{\lambda^2} . \qquad (3.3)$$

Since the lattice constants, a, b, and c, of nickel dimethylglyoxime are known to be 16.68, 10.44, and 6.50 A.U. respectively (36), values of $\frac{4\sin^2\theta}{\lambda^2}$ were calculated for each possible combination of h, k, and l, and compared with the values obtained from the powder pattern. Where agreement was found these values of h, k, and l, were assigned to that reflection. In Figure 9 the diffraction patterns of nickel

Figure 9. Diffraction pattern of powdered nickel dimethylglyoxime, top photograph, and nickel 3-methylnioxime, bottom photograph



dimethylglyoxime and of nickel 3-methylnioxime are reproduced. The assignments for the photograph of nickel dimethylglyoxime are shown in Table 14. The lines 2 and 13 in this photograph are the (002) reflection for which n = 1, and the (004) reflection for which n = 2. Usually the (004) reflection was not visible and the -Ni-Ni- bond length was calculated from the (002) line.

The linear distance between lines was measured accurately, and the angle θ calculated from the equation

$$\theta = \frac{180\ s}{4\ \pi\ R}\ . \qquad (3.4)$$

Then

$$d' = \frac{n\lambda}{2\ \sin\ \theta}\ . \qquad (3.5)$$

R is the camera radium, which was measured in each case from the distance between the centers of the two holes in the photograph.

In Table 15 values of the nickel-nickel distance obtained from the powder method are compared with those obtained by the more accurate back reflection method using single crystals. These data show that the powder method is accurate to about ± 0.03 A.U.

The apparent metal-metal bond lengths and the data from which they were calculated are shown in Table 16.

Table 14. Assignment of reflections in the powder photograph of nickel dimethylglyoxime

Line	s	θ	$\frac{4 \sin^2 \theta}{\lambda^2}$ measured	$\frac{4 \sin^2 \theta}{\lambda^2}$ calculated	(hkl)
1	3.895	9°47'	0.0486	-	-
2	5.495	13°47'	0.0955	0.0956	(002)
3	5.865	14°44'	0.109	0.108	(112)
4	7.000	17°35'	0.154	0.153	(402)
5	7.210	18°07'	0.163	0.161	(240)
6	7.790	19°34'	0.189	0.189	(422)
7	8.715	21°53'	0.234	-	-
8	9.245	23°13'	0.261	0.257	(242)
9	9.670	24°17'	0.284	0.282	(413)
10	9.995	25°07'	0.303	-	-
11	10.475	26°19'	0.331	-	-
12	10.970	27°33'	0.360	0.365	(143)
13	11.375	28°34'	0.385	0.382	(004)
14	11.620	29°11'	0.400	0.397	(204)

Table 15. Comparison of metal-metal bond lengths from the powder method with those from the back reflection method using single crystals

Complex	-M-M- length, powder method	-M-M- length, back ref. method	Error
nickel dimethylglyoxime	3.236	3.233	+0.003
nickel nioxime	3.236	3.237	-0.001
nickel α-furildioxime	3.427	3.448	-0.021
nickel α-benzildioxime	3.561	3.547	+0.014
nickel heptoxime	3.571	3.596	-0.025

Table 16. Calculation of metal-metal bond lengths from powder photographs

Complex	s	θ	r	d'
nickel dimethylglyoxime	5.490	13°47'	5.692	3.236
nickel nioxime	5.485	13°47'	5.707	3.236
nickel α-furildioxime	5.175	13°00'	5.703	3.427
nickel α-benzildioxime	4.975	12°30'	5.703	3.561
nickel heptoxime	4.978	12°28'	5.727	3.571
nickel 4-methylnioxime	5.490	13°47'	5.717	3.236
nickel 4-isopropylnioxime	5.585	14°00'	5.710	3.187
nickel 4-*tert*-amylnioxime	5.600	14°00'	5.727	3.187
nickel 3-methylnioxime	5.120	12°50'	5.712	3.471

D. Measurement of Absorption Spectra and Molar Absorptivities in Organic Solvents

Solutions of known concentration were prepared by weighing the solid complex accurately on a micro-balance, and transferring to a 100-ml. class A volumetric flask with the solvent to be used. About 60 ml. of solvent was then added and the solid dissolved with the aid of heat. After dissolution was complete the flask was filled almost to the mark. Final dilution to exactly 100 ml. was not made until just before the absorption measurements were made. Care was taken to keep loss of solvent by evaporation to a minimum. The solutions were transferred as quickly as possible and all absorption cells used had glass stoppers.

Spectra were scanned on an automatic recording Model 14 Cary Spectrophotometer. For chloroform solutions, and with 1.00-cm. cuvettes, the region scanned was from 240 mμ to 550 or 650 mμ, depending on the intensity of absorption of each complex in the visible region. 1,2-Dichlorobenzene solutions were scanned from 360 mμ to 520 or 550 mμ.

For the measurement of molar absorptivities of bands a Beckman DU spectrophotometer with photomultiplier was used. With this instrument, cooling water was circulated through the lamp housing to prevent heating in the cell compartment. The molar absorptivities are reported in Table 17.

The chloroform used was reagent-grade quality. Eastman "white label" 1,2-dichlorobenzene (99 + % purity) was steam distilled once, separated, dried over calcium sulfate, and then triply distilled through a Vigreaux column.

Table 17. Molar absorptivities of some nickel and palladium complexes dissolved in chloroform and in 1,2-dichlorobenzene

Complex	Chloroform sol'n		1,2-Dichlorobenzene	
	$\lambda_{max.}$	$\epsilon_{max.}$	$\lambda_{max.}$	$\epsilon_{max.}$
nickel dimethylglyoxime	262	2.45×10^4	377	3.38×10^3
	327	4.58×10^3		
	374	3.43×10^3		
nickel nioxime	265	2.35×10^4	386	3.70×10^3
	333	5.02×10^3		
	383	3.57×10^3		
nickel α-furildioxime	293	3.90×10^4	438	1.48×10^4
	384	1.04×10^4		
	435	1.52×10^4		
nickel α-benzildioxime	273	4.03×10^4	409	1.10×10^4
	361	9.89×10^3		
	406	1.09×10^4		
nickel heptoxime	263	2.49×10^4	379	3.96×10^3
	330	5.05×10^3		
	377	4.05×10^3		
palladium dimethylglyoxime	242	2.22×10^4		
	275	1.26×10^4		
	374	1.81×10^3		

Table 17. (Continued)

Complex	Chloroform sol'n $\lambda_{max.}$	Chloroform sol'n $\epsilon_{max.}$	1,2-Dichlorobenzene $\lambda_{max.}$	1,2-Dichlorobenzene $\epsilon_{max.}$
palladium nioxime	242	2.74×10^4		
	274	1.39×10^4		
	383	1.95×10^3		
palladium heptoxime	243	2.13×10^4		
	278	1.37×10^4		
	370	1.87×10^3		
palladium α-furildioxime	252	2.47×10^4		
	285	4.11×10^4		
	379	2.00×10^4		
palladium α-benzildioxime	245	3.27×10^4		
	267	3.56×10^4		
	324	1.96×10^4		

E. Absorption Spectra of Colloidal Suspensions of the Nickel and Palladium Complexes

When a vic-dioxime is added to a solution containing either nickel or palladium ions at the proper pH, a finely divided precipitate is obtained which coagulates after standing for a few minutes. However, if the precipitation is carried out in the presence of a protective colloid, that is, some substance which prevents the coagulation of colloidal particles, then a stable colloidal suspension is obtained. These suspensions are stable for several weeks. D. Hooker (45) determined the size of the particles by means of an electron microscope and found them to be 20 X 2000 millimicrons, which is in the colloidal range.

A known amount of nickel(II) perchlorate or of palladium(II) perchlorate was added to a 100-ml. volumetric flask and either 10 ml. of 10% gum arabic or 10 ml. of 1% gelatin solution was added as the protective colloid. The vic-dioxime was then added in about 50% excess, followed by two drops of 2 M ammonium hydroxide, and water added almost to the mark. After one hour at room temperature the solution was diluted to 100 ml. and the absorption spectrum measured on the Cary Model 14 recording spectrophotometer, using 1.00-cm. cuvettes. α-Benzildioxime is so insoluble in water that it was necessary to use a large amount of the hot saturated solution and to scan the spectrum with 5.00- and 10.00-cm. cells. In this case the molar absorptivity could not be estimated because it was not certain that all the nickel(II) had been converted to the complex.

The absorption spectrum of a given complex was found to be the same whether the protective colloid used was gum arabic or gelatin.

F. Measurement of the Absorption Spectra of Single Crystals

Two methods were used to measure the absorption of plane polarized light by crystals of the nickel and palladium complexes. The first method used was essentially that of Tsuchida and Kobayashi (88) in which a polarizing microscope, mounted horizontally, is used to project an image of the crystal on the slit of a spectrograph. The spectrum is recorded on a photographic plate. Several exposures are made at different time intervals with the crystal in the light path and with the crystal removed from the light path. At wavelengths where the blackening of the photographic plate is the same it is possible to calculate the absorbancy of the crystal from the ratio of the lengths of time of exposure by means of the equation

$$A = \frac{0.9}{t} \log \frac{\tau}{\tau'} , \qquad (3.6)$$

where t is the thickness of the crystal in millimeters, τ is the time of exposure with the crystal in the light path, and τ' is the time of exposure with the crystal removed from the light path.

The second method, which gives better resolution and is less tedious, makes use of a microscope attachment for the Model 112 Perkin-Elmer Infrared spectrophotometer. Since the visible region of the spectrum was of interest, a tungsten light source was used and a photomultiplier tube for the detector. A schematic diagram of the optics are shown in Figure 10.

The extremely small size of the crystals available made the measurement of their absorption spectra difficult, and in fact, it was necessary to lay about three crystals side by side in order to get enough light through to the detector. Although the spectra reported in this work were determined by the photographic method, the spectrophotometric method would be recommended for any future measurements.

G. Measurement of Solubility in Organic Solvents

In this research two different methods were used to measure the solubilities in organic solvents.

1. Method A

Saturated chloroform solutions were prepared by placing an excess of the solid complex in about five milliliters of reagent-grade chloroform in a tightly corked test tube, and shaking on a mechanical shaker for 24 hours in a room maintained at 25°C. When equilibrium was reached the solutions were centrifuged and a one milliliter aliquot of the supernatant liquid taken with a pipette. This aliquot was diluted in a volumetric flask to a convenient concentration to measure the absorbancy with a spectrophotometer.

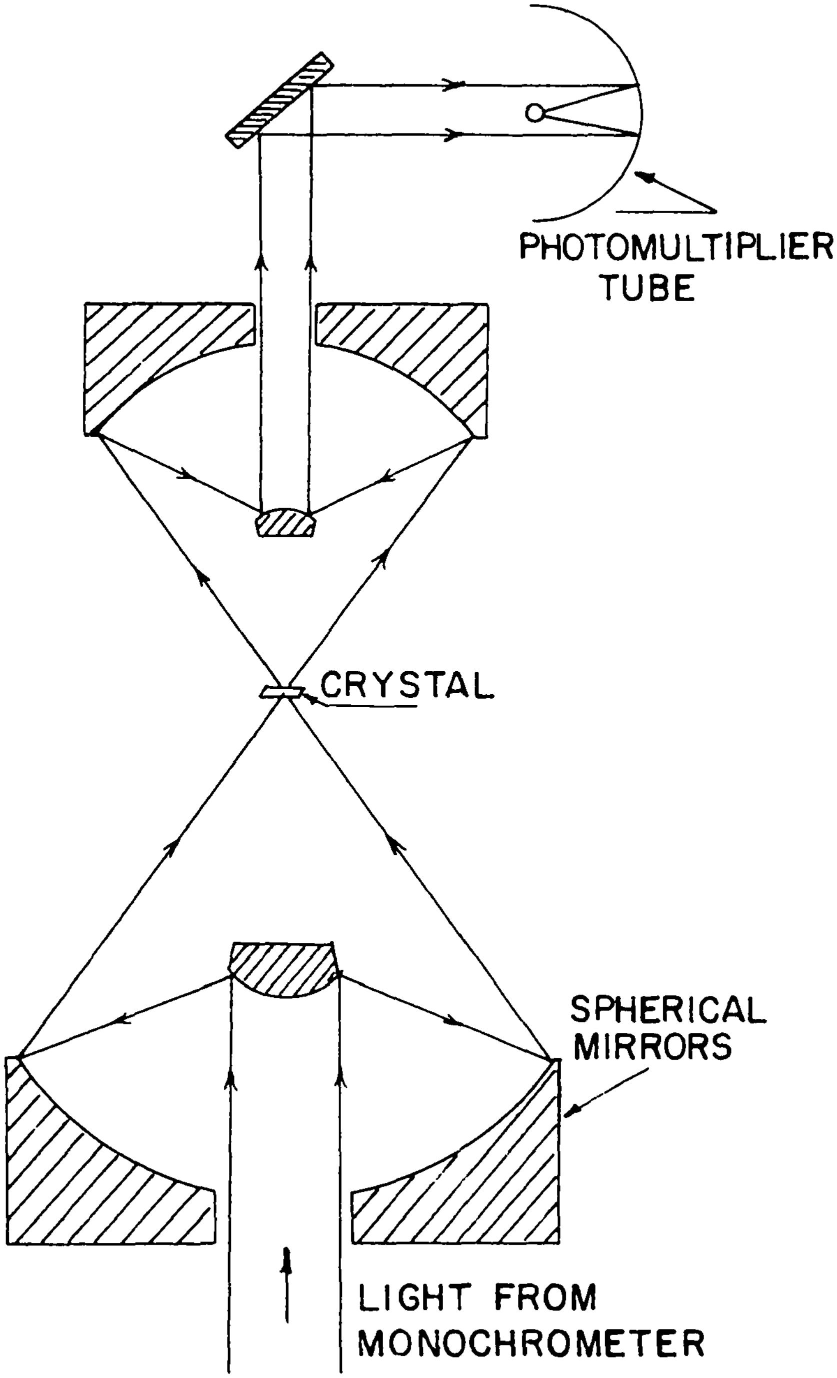

PHOTOMULTIPLIER TUBE
CRYSTAL
SPHERICAL MIRRORS
LIGHT FROM MONOCHROMETER

Figure 10. Schematic diagram of optics of reflecting microscope for measuring absorption spectra of single crystals

2. Method B

The solubilities of the nickel complexes in 1,2-dichlorobenzene and of the palladium complexes in chloroform were determined in the following manner: A slight excess of the solid complex was added to the hot solvent (boiling chloroform or 1,2-dichlorobenzene at about 100°C.). The heat was maintained for a minute with swirling, and then the mixture was set aside in a dark cabinet for 24 to 48 hours in a room maintained at 25°C. After equilibrium was reached the excess solid was removed by filtering. To keep evaporation of the solvent to a minimum a fast filter paper was used, the funnel was kept covered with a watch glass, and the filtrate was caught in a 25-ml. volumetric flask in which the funnel stem almost completely filled the neck of the flask. An aliquot of the filtrate was diluted to a convenient concentration to measure the absorbancy on a spectrophotometer.

Some representative data are given in Tables 17, 18 and 19.

H. Measurement of Solubility in Water

To measure the solubility in water at 25°C. an excess of the crystalline solid was added to about 100 ml. of boiled and deionized water. This mixture was shaken at 25.0°C. for nine days, filtered, and an aliquot of the

Table 18. Determination of solubilities of some nickel complexes in chloroform

Complex	Dilution	Wavelength in mμ	Molar Absorbtivity	Solubility (moles/l.)
nickel dimethylglyoxime	1 ml. to 25 ml.[a]	327	4.58 X 10^3	5.5 (± 0.3) X 10^{-4}
nickel nioxime	1 ml. to 10 ml.[a]	265	2.35 X 10^4	0.67 (± 0.08) X 10^{-4}
nickel α-furildioxime	1 ml. to 50 ml.[a]	384	1.04 X 10^4	16 (± 0.5) X 10^{-4}
nickel α-benzildioxime	1 ml. to 50 ml.[a]	361	9.89 X 10^3	13 (± 0.5 X 10^{-4}
nickel heptoxime	1 ml. to 50 ml.[a]	377	4.05 X 10^3	56 (± 1) X 10^{-4}

[a] 1.00-cm. cuvettes were used in each case.

Table 19. Determination of solubilities of some nickel complexes in o-dichlorobenzene

Complex	Dilution	Wavelength in mμ	Molar Absorptivity	Solubility (moles/l.)
nickel dimethylglyoxime	none[a]	377	3.38 X 10^3	2.0 (± 0.04) X 10^{-4}
nickel nioxime	none[a]	386	3.70 X 10^3	0.32 (± 0.01) X 10^{-4}
nickel α-furildioxime	1 ml. to 50 ml.[a]	437.5	1.48 X 10^4	18 (± 1.4) X 10^{-4}
nickel α-benzildioxime	2 ml. to 25 ml.[a]	409	1.10 X 10^4	5.9 (± 0.5) X 10^{-4}
nickel heptoxime	2 ml. to 25 ml.[a]	379	3.96 X 10^3	13 (± 0.7) X 10^{-4}

[a] 1.00-cm. cuvettes were used in each case.

Table 20. Determination of solubilities of some palladium complexes in chloroform

Complex	Dilution	Wavelength in mμ	Molar Absorptivity	Solubility
palladium nioxime	none[a]	384	1.94 X 10^3	1.4 (± 0.2) X 10^{-4}
palladium dimethylglyoxime	10 ml. to 25 ml.[a]	375	1.79 X 10^3	5.0 (± 0.4) X 10^{-4}
palladium heptoxime	5 ml. to 100 ml.[a]	370	1.87 X 10^3	8.1 (± 0.5) X 10^{-4}
palladium α-furildioxime	5 ml. to 100 ml.[a]	379	1.99 X 10^4	8.5 (± 0.3) X 10^{-4}
palladium α-benzildioxime	5 ml. to 25 ml.[a]	395	2.12 X 10^3	89 (± 13) X 10^{-4}

[a] 1.00-cm. cuvettes were used in each case.

filtrate analyzed spectrophotometrically by the method of Ferguson and Banks (29). Because of the low solubilities, a 50.0-ml. aliquot was transferred to a 100-ml. volumetric flask, the color developed, and the absorbancy measured using 10.0-cm. cells.

I. Measurement of Solubility Products

Solubility products were measured in water at 25.0° and at 40.0°C. Three methods were tried, which are discussed below as Methods A, B, and C.

For temperature control a thermostated water bath was used that maintained the temperature within 0.05°C. of the desired temperature. A mechanical shaker was arranged with its arms over the water bath so the solutions, which were contained in 100- or 200-ml. volumetric flasks, could be shaken continuously while immersed in the constant temperature bath.

1. Method A

This method was used independently by Christopherson and Sandell (22) and by Babko and Mikhelson (4) to determine the solubility product of nickel dimethylglyoxime at 25°C. An excess of solid complex was shaken with a moderately acidic buffer solution. After equilibration the excess solid was filtered off and the amount of dissolved nickel determined. Christopherson and Sandell determined the nickel colorimetrically and Babko and Mikhelson determined it gravimetrically. Then, knowing the ionization constant for the vic-dioxime and the pH of the solution at equilibrium one can calculate the solubility product.

It was observed in this work, and also by Christopherson and Sandell (22) that when one adds the dried complex to a buffer solution the system reaches equilibrium very slowly. However, if the complex is not allowed to dry after it is precipitated, equilibration occurs much more rapidly. Therefore, some of each complex to be studied was precipitated, washed six times with water, separating the precipitate by centrifugation, and stored under water. When some of the complex was desired for a measurement of the solubility product it was separated by filtering through a micro-Buchner funnel, washed with a few drops of water, and transferred to a 200-ml. volumetric flask while still wet. Then, 100 ml. of solvent solution was added.

The solvents consisted of HCl-KCl buffer solutions which were 0.0100 M, 0.00500 M, 0.00100 M, 0.000500 M, and 0.000100 M in hydrochloric acid and contained enough potassium chloride to make the ionic strength 0.05000 M. A sixth solution was prepared which was 0.0500 M in potassium chloride.

The mixture of solid complex and solvent was placed on a shaker so that it was immersed in the constant temperature bath and shaken for three to six hours. After equilibration the undissolved complex was removed by filtering, with suction, through a sintered glass disc of medium porosity. The type of filter used, shown in Figure 11, permitted this operation to be carried out in the temperature bath.

With a pipette an aliquot of the filtrate was taken and analyzed spectrophotometrically by the method of Ferguson and Banks (29). The pipette was checked to see what volume of water at 40.0°C. it would deliver. It was found that no correction was necessary. The remaining portion of the filtrate was used to measure the pH of the solution.

Since _vic_-dioximes slowly hydrolyze in acid solution, Christopherson and Sandell (22) measured the solubility in solutions saturated with dimethylglyoxime so that any hydrolysis would be negligible. They also made some measurements in solutions that were not saturated with the dioxime and found the same value of the solubility product. Babko and Mikhelson (4) state that the solubility does not change any more after six hours and that during this time no appreciable hydrolysis of dimethylglyoxime takes place at pH 3.0 and 3.5.

However, at 40°C. the rate of hydrolysis will have increased by about three times. It was found that under the most acidic conditions encountered appreciable hydrolysis of heptoxime would occur in half an hour. As the pH was decreased in order to prevent hydrolysis it appeared that

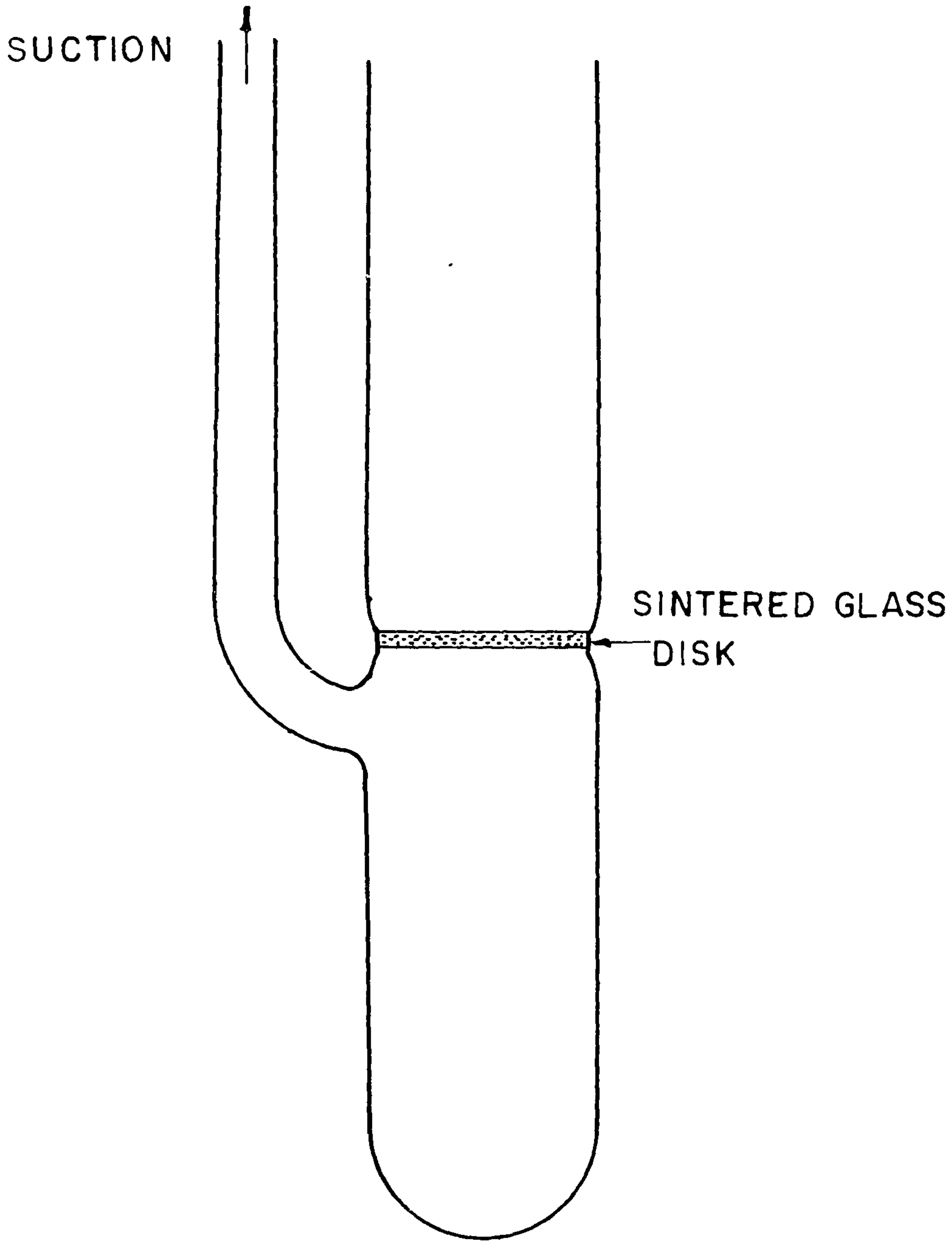

SUCTION
SINTERED GLASS DISK

Figure 11. Apparatus for filtering solutions at constant temperature

longer periods of shaking were required to reach equilibrium so that one still could not be sure that this source of error was eliminated. Furthermore, hydrolysis of nioxime and heptoxime could not be avoided by measuring the solubility in a solution saturated with the free dioxime since this would reduce the concentration of nickel to about 10^{-9} moles per liter; a quantity too small to measure.

The solubility product is calculated in the following manner: The reactions to be considered are:

$$Ni(DH)_2 = Ni^{++} + 2\ DH^-$$

and

$$DH_2 = H^+ + DH^- ,$$

where DH_2, as before, represents the free dioxime with two ionizable hydrogen atoms. The solubility product is given by

$$K_{sp} = a_{Ni^{++}} \cdot a^2_{DH^-} \tag{3.7}$$

and the ionization constant by

$$K_{DH_2} = \frac{a_{H^+} \cdot a_{DH^-}}{a_{DH_2}} \ . \tag{3.8}$$

Solving Equation 3.8 for a_{DH^-} and substituting this into Equation 3.7 gives

$$K_{sp} = a_{Ni^{++}} \cdot K_{DH_2}^2 \frac{a_{DH_2}^2}{a_{H^+}^2} \quad . \tag{3.9}$$

Also,

$$a_i = \frac{c_i}{f_i} \quad , \tag{3.10}$$

and

$$S = c_{Ni^{++}} = 1/2 \, c_{DH_2} \quad . \tag{3.11}$$

Thus, Equation 3.9 becomes

$$K_{sp} = K_{DH_2}^2 \frac{4 \, S^3 \, f_{Ni^{++}}}{a_{H^+}^2} \tag{3.12}$$

The value of the activity coefficient of nickel ions was estimated from the second approximation to the Debye-Hückel equation:

$$\log f_i = \frac{A \, z_i^2 \sqrt{\mu}}{1 + \alpha_i B \sqrt{\mu}} \tag{3.13}$$

for which α_i for Ni^{++} was taken to be 6 X 10^{-8} (51, 53), A = 0.5092 at 25.0°C., 0.5241 at 40.0°C., and B = 0.3286 X 10^8 at 25.0°C. and 0.3318 X 10^8 at 40.0°C. (8, 57). Values of the ionization constants of dimethylglyoxime, nioxime, and heptoxime at 25.0°C. were taken from the work of Banks and Carlson (5). Values at 40.0°C. were determined in the course of this work and are discussed later. For dimethylglyoxime, nioxime, and heptoxime at 25.0°C., $K_{DH_2} = 2.5 \times 10^{-11}$, 2.5×10^{-11}, and 2.0×10^{-11} respectively, and at 40.0°C., 3.0×10^{-11}, 3.1×10^{-11}, and 3.4×10^{-11}. (See also Table 27, p.84.)

2. Method B

The second method tried was that of Wenger, *et al.* (92). In this method the solubility product is calculated from the pH at which the nickel complex just begins to precipitate.

Between 0.100 and 1.00 ml. of 0.0229 M nickel chloride was added to 10.00 ml. of 0.1000 N hydrochloric acid. A measured volume of the dioxime (0.0458 M nioxime; 0.0229 M heptoxime) was then added. The nickel and the dioxime were present in stoichiometric amounts in some cases and in others one of the reagents was in excess. Immediately after the dioxime was added the solution was placed in the constant temperature bath and 0.1000 N sodium hydroxide slowly added from a burette until the appearance of a definite color due to precipitation of the nickel complex. It can be shown that the solubility product is then given by the expression

$$K_{sp} = f_{Ni^{++}} \left[m_{Ni^{++}} - c_{Ni(DH)_2} \right] \left[\frac{m_{DH_2} - 2\, c_{Ni(DH)_2}}{\dfrac{1}{f_{DH^-}} + \dfrac{a_{H^+}}{K_{DH_2}\, f_{DH_2}}} \right]^2 \qquad (3.14)$$

where m_i is the total concentration of an atom or group of atoms, irregardless of the particular species in which it exists, and $c_{Ni(DH)_2}$ may be thought of as the concentration of nickel dimethylglyoxime if it were dissolved rather than being suspended in the medium. The other symbols have already been explained.

Wenger et al. (92) assumed that $c_{Ni(DH)_2}$ is negligibly small. In this work it was estimated by measuring the absorbancy at the wavelength of maximum absorption of the particular complex in colloidal suspension. The value of $c_{Ni(DH)_2}$ was then calculated from the known molar absorptivity. It was found that this term resulted in only a small correction which, in view of the poor accuracy obtainable by this method, is indeed negligibly small.

Furthermore, $1/f_{DH^-}$ is small compared to $a_{H^+}/(K_{DH_2}\ f_{DH_2})$ and $f_{DH_2} \doteq 1$, so that Equation 3.14 can be rewritten as:

$$K_{sp} = f_{Ni^{++}}\ m_{Ni^{++}}\ K^2_{DH_2} \left[\frac{m_{DH_2}}{a_{H^+}} \right]^2 \quad . \qquad (3.15)$$

The precision obtainable by this method is very poor. In a series of ten determinations the solubility product varied over a range of 100 units. The reason for the poor results are due, at least in part, to the facts that the color of the nickel precipitate appears gradually so that the end point is hard to determine, and the end point depends on the rate of addition of sodium hydroxide.

3. Method C

The method which gave the best precision was simply to mix nickel chloride and the vic-dioxime in stoichiometric amounts, shake for two hours at the desired temperature in order to achieve complete precipitation, and then measuring the pH accurately.

Between 0.100 and 1.00 ml. of 0.0229 M nickel chloride was added by means of a micro-pipette to a solution containing just enough vic-dioxime to react with all the nickel (prepared from 0.0458 M nioxime, 0.0229 M heptoxime, or 0.00229 M dimethylglyoxime) the total volume of which was adjusted to about 20 ml. by adding a known amount of water. The total volume was taken as the sum of the volumes of water, nickel chloride solution, and vic-dioxime solution. The dioxime solution was placed in the temperature bath about two minutes before the nickel solution was added. The mixture was then shaken for at least two hours in order to insure complete precipitation, and then the pH of the mixture determined without filtering. To determine the pH, a model GS pH meter was used.

If m_{Ni} is the total amount of nickel present, and m_{DH_2} is the total amount of vic-dioxime present at equilibrium, expressed in moles per liter, then $2\ m_{Ni} = m_{DH_2}$, since nickel chloride and the vic-dioxime are added in stoichiometric amounts. Further,

$$m_{Ni} = c_{Ni} + c_{Ni(DH)_2} \qquad (3.16)$$

$$m_{DH_2} = c_{DH^-} + c_{DH_2} + 2\ c_{Ni(DH)_2} \qquad (3.17)$$

where c_i represents the molar concentration of species i. Since the solution is electrically neutral

$$c_{H^+} + 2\ c_{Ni^{++}} = c_{Cl^-} + c_{DH^-} \quad . \qquad (3.18)$$

$$c_{Cl^-} = 2\ m_{Ni} \qquad (3.19)$$

$$c_i = \frac{a_i}{f_i} \qquad (3.10)$$

$$\frac{a_{H^+}}{f_{H^+}} + 2\ c_{Ni^{++}} = 2\ m_{Ni} + \frac{a_{DH^-}}{f_{DH^-}} \quad . \qquad (3.20)$$

Eliminate $c_{Ni(DH)_2}$ between Equations 3.16 and 3.17.

$$2\ c_{Ni^{++}} = c_{DH^-} + c_{DH_2} \qquad (3.21)$$

The ionization constant of the vic-dioxime is given by

$$K_{DH_2} = \frac{a_{H^+} \cdot a_{DH^-}}{a_{DH_2}} \qquad (3.22)$$

$$a_{DH_2} = c_{DH_2} \cdot f_{DH_2} = \frac{a_{H^+} \cdot a_{DH^-}}{K_{DH_2}} \qquad (3.23)$$

Substituting this result into Equation 3.15:

$$2\ c_{Ni^{++}} = c_{DH^-} + \frac{a_{H^+} \cdot c_{DH^-} \cdot f_{DH^-}}{K_{DH_2} \cdot f_{DH_2}} \qquad (3.24)$$

Eliminate 2 $c_{Ni^{++}}$ between Equations 3.20 and 3.24.

$$\frac{a_{H^+} \cdot a_{DH^-}}{K_{DH_2} \cdot f_{DH_2}} = 2\ m_{Ni} - \frac{a_{H^+}}{f_{H^+}} \qquad (3.25)$$

$$a_{DH^-} = \frac{K_{DH_2} \cdot f_{DH_2}}{a_{H^+}} \left[2\ m_{Ni} - \frac{a_{H^+}}{f_{H^+}} \right] \qquad (3.26)$$

Substituting this expression for a_{DH^-} into Equation 3.20;

$$\frac{2\ a_{Ni^{++}}}{f_{Ni^{++}}} = 2\ m_{Ni} - \frac{a_{H^+}}{f_{H^+}} + \frac{K_{DH_2} \cdot f_{DH_2}}{a_{H^+} \cdot f_{DH^-}} \left[2\ m_{Ni} - \frac{a_{H^+}}{f_{H^+}} \right] \qquad (3.27)$$

The third term on the right hand side of this equation is negligibly small. Neglecting this term and solving for $a_{Ni^{++}}$:

$$a_{Ni^{++}} = m_{Ni} f_{Ni^{++}} - \frac{a_{H^+} \cdot f_{Ni^{++}}}{2\ f_{H^+}} \qquad (3.28)$$

Since the solubility product is $K_{sp} = a_{Ni^{++}} \cdot a^2_{DH^-}$, it can be evaluated from Equations 3.26 and 3.28.

In all three of the methods for measuring the solubility product the presence of the species $Ni(DH)^+$ has been ignored. For Method C the following equation can be derived in which this species is taken into account:

$$K_{sp} = \frac{K^2_{DH_2}}{a^2_{H^+}} \left[\frac{2\, m_{Ni} + \dfrac{K_{DH_2}}{a_{H^+} \cdot f_{DH^-}} (2\, m_{Ni} - c_{H^+}) - c_{H^+}}{\dfrac{2}{f_{Ni^{++}}} + \dfrac{K_1\, K_{DH_2}}{a_{H^+} \cdot f_{NiDH^+}} (2\, m_{Ni} - c_{H^+})} \right] (2\, m_{Ni} - c_{H^+})^2 \qquad (3.29)$$

where

$$K_1 = \frac{a_{NiDH^+}}{a_{Ni^{++}} \cdot a_{DH^-}} \qquad (3.30)$$

Substituting numbers from actual data into Equation 3.29 it can easily be shown that in order for the species $NiDH^+$ to make a significant contribution to the solubility product, K_1 must be smaller than about 10^{10}. Charles and Freiser (21) report a value of 2.76×10^{10} for K_1 in 50% dioxane-water at 25.0°C. Furthermore, their data show that this constant does not change appreciably between 25 and 40°C. In water, one would expect the value of K_1 to be even smaller because of the higher dielectric constant. Thus, it appears that a small correction might be necessary in a very accurate determination of the solubility product. In the present determinations however, it is, in all probability, less than experimental error.

Values of the solubility products obtained by this method are reported in Tables 21 to 26.

Table 21. Determination of the solubility product of nickel dimethylglyoxime in water at 25°C.

m_{Ni} X 10^4	pH	a_{H^+} X 10^4	μ X 10^4	K_{sp}
1.036	4.64	0.231	2.99	3.3×10^{-24}
2.385	4.04	0.904	6.70	1.9×10^{-24}
2.827	3.94	1.14	7.91	1.9×10^{-24}
5.585	3.55	2.82	15.3	1.8×10^{-24}
10.90	3.17	6.73	29.3	1.7×10^{-24}
2.385	4.08	0.823	6.740	2.5×10^{-24}
2.827	3.97	1.08	7.94	2.3×10^{-24}
5.585	3.56	2.74	15.4	2.2×10^{-24}
5.585	3.56	2.78	15.4	2.1×10^{-24}
10.90	3.17	6.73	35.4	2.0×10^{-24}
			Average	2.2×10^{-24}

Table 22. Determination of the solubility product of nickel dimethylglyoxime in water at 40°C.

$m_{Ni} \times 10^4$	pH	$a_{H^+} \times 10^4$	$\mu \times 10^4$	K_{sp}
2.827	4.12	0.766	8.10	9.9×10^{-24}
10.90	3.29	5.09	33.15	7.3×10^{-24}
2.385	4.24	0.581	6.86	8.5×10^{-24}
2.827	4.14	0.730	8.12	8.4×10^{-24}
5.585	3.65	2.25	15.6	4.9×10^{-24}
10.90	3.21	6.14	29.6	3.2×10^{-24}
2.385	4.16	0.698	6.81	5.4×10^{-24}
2.827	4.03	0.933	8.01	4.6×10^{-24}
5.585	3.58	2.62	15.4	3.2×10^{-24}
10.90	3.21	6.14	29.6	3.3×10^{-24}
			Average	5.9×10^{-24}

Table 23. Determination of the solubility product of nickel nioxime in water at 25°C.

$m_{Ni} \times 10^4$	pH	$a_{H^+} \times 10^4$	$\mu \times 10^4$	K_{sp}
2.245	3.39	4.11	4.68	4.9×10^{-29}
2.793	3.29	5.13	5.82	7.2×10^{-29}
5.452	2.99	10.2	11.3	3.3×10^{-29}
5.452	2.99	10.2	11.3	3.3×10^{-29}

Table 23. (Continued)

m_{Ni} X 10^4	pH	a_{H^+} X 10^4	μ X 10^4	K_{sp}
10.41	2.71	19.5	21.5	3.2×10^{-29}
0.208	3.12	7.60	500	1.9×10^{-29}
0.642	2.41	39.0	500	2.1×10^{-29}
1.48	2.12	76.0	500	6.9×10^{-29}
2.245	3.39	4.05	4.71	6.3×10^{-29}
2.793	3.29	5.09	5.83	4.0×10^{-29}
5.452	3.00	10.00	11.3	1.6×10^{-29}
			Average	4.1×10^{-29}

Table 24. Determination of the solubility product of nickel nioxime in water at 40.0°C.

m_{Ni} X 10^4	pH	a_{H^+} X 10^4	μ X 10^4	K_{sp}
14.5	1.20	630.0	886	1.2×10^{-27}
1.16	2.70	20.0	523	0.73×10^{-27}
10.8	1.47	339.0	662	0.84×10^{-27}
2.245	3.44	3.63	4.92	1.4×10^{-27}
2.793	3.34	4.62	6.07	1.1×10^{-27}
5.452	3.03	9.29	11.7	0.84×10^{-27}
10.41	2.75	17.9	22.3	0.82×10^{-27}

Table 24. (Continued)

m_{Ni} X 10^4	pH	a_{H^+} X 10^4	μ X 10^4	K_{sp}
1.134	3.75	1.77	2.02	1.5 X 10^{-27}
2.245	3.43	3.68	4.09	1.2 X 10^{-27}
2.793	3.34	4.59	5.09	1.3 X 10^{-27}
5.452	3.04	9.16	10.0	1.3 X 10^{-27}
10.41	2.74	18.11	19.5	0.62 X 10^{-27}
			Average	1.1 X 10^{-27}

Table 25. Determination of the solubility product of nickel heptoxime in water at 25°C.

m_{Ni} X 10^4	pH	a_{H^+} X 10^4	μ X 10^4	K_{sp}
2.223	3.48	3.34	5.00	1.9 X 10^{-27}
2.759	3.38	4.14	6.21	2.3 X 10^{-27}
5.326	3.07	8.47	11.7	1.3 X 10^{-27}
5.326	3.09	8.15	11.9	3.3 X 10^{-27}
9.956	2.79	16.1	21.8	2.6 X 10^{-27}
5.05	2.16	69.2	500	2.1 X 10^{-27}
			Average	2.3 X 10^{-27}

Table 26. Determination of the solubility product of nickel heptoxime in water at 40.0°C.

m_{Ni} X 10^4	pH	a_{H^+} X 10^4	μ X 10^4	K_{sp}
2.223	3.54	2.86	4.13	2.3 X 10^{-26}
2.759	3.46	3.49	6.53	3.0 X 10^{-26}
1.128	3.89	1.29	2.74	2.6 X 10^{-26}
2.223	3.52	3.01	5.16	1.4 X 10^{-26}
2.759	3.41	3.91	6.32	1.1 X 10^{-26}
5.326	3.11	7.83	12.1	1.2 X 10^{-26}
9.956	2.82	14.7	22.5	1.7 X 10^{-26}
16.5	1.56	276	419	1.4 X 10^{-26}
			Average	1.8 X 10^{-26}

J. Measurement of Acid Dissociation Constants of *vic*-Dioximes

The acid dissociation constants of dimethylglyoxime, nioxime, and heptoxime were measured in water at 40.0°C. The method used involved the measurement of the solubility of the dioxime in basic solutions, as described by Christopherson and Sandell (22), and by Babko and Mikhelson (3).

Sodium bicarbonate - sodium hydroxide buffer solutions ranging in pH from 9.60 to 11.00 were prepared by the method of Bates and Bower (9). For dimethylglyoxime, 100 ml. of buffer was added to an excess of the solid dioxime in a 200-ml. volumetric flask. For nioxime and heptoxime, 50 ml. of buffer solution was added to the excess solid. This mixture was placed on the shaker and maintained at 40.0°C. for two hours. After equilibration the excess solid was filtered off and the pH measured with a Beckman model GS pH meter. The solution was maintained at 40.0°C. while filtering and measuring the pH. An aliquot of the solution at 40° was taken with a pipette, diluted, and the dioxime determined gravimetrically.

For dimethylglyoxime a 50.0-ml. aliquot was taken, and for nioxime and heptoxime, 10.0 ml. aliquots were taken. The pipettes used were calibrated for water at 40.0°C. and it was found that no correction was necessary. That is, the pipettes deliver the nominal volume of water at 40.0°C.

Dioximes are dibasic acids, ionizing according to the equations

$$DH_2 = DH^- + H^+$$

$$DH^- = D^= + H^+$$

where DH_2 represents the un-ionized dioxime. The equilibrium constants are:

$$K_{DH_2} = \frac{a_{DH^-} \cdot a_{H^+}}{a_{DH_2}} \qquad (3.31)$$

$$K_{DH^-} = \frac{a_{D^=} \cdot a_{H^+}}{a_{DH^-}} \qquad (3.32)$$

The solubility, S, can be expressed as

$$S = c_{DH_2} + c_{DH^-} + c_{D^=} , \qquad (3.33)$$

but the concentration of $D^=$ is negligibly small and may be neglected. Solving Equation 3.31 for c_{DH^-} and substituting this result into Equation 3.33, one obtains the expression

$$S = c_{DH_2} + \frac{K_{DH_2} \cdot c_{DH_2}}{a_{H^+} \cdot f_{DH^-}} . \qquad (3.34)$$

The activity coefficient of the un-ionized dioxime, f_{DH_2}, is taken as unity. Christopherson and Sandell (22) estimated this activity coefficient to be 1.02 in water of ionic strength 0.0500 M and 25°C. Neglecting this introduces an error of about 2%, which is less than experimental error.

According to Equation 3.34 a plot of solubility against $1/(a_{H^+} \cdot f_{DH^-})$ will give a straight line which intersects the ordinate axis at c_{DH_2} and has a slope equal to $K_{DH_2}\ c_{DH_2}$, thereby permitting the calculation of the first ionization constant of the dioxime.

The calculations are complicated by the facts that the ionic strength is different for each solution and that the ionic strength of each buffer changes as it dissolves dioxime.

For each solution, the ionic strength was estimated in the following manner:

The equilibria controlling the pH are:

$$H_2CO_3 \;=\; HCO_3^- \;+\; H^+$$

and

$$HCO_3^- \;=\; CO_3^= \;+\; H^+$$

for which we have the following equilibrium constants:

$$K_1 \;=\; \frac{a_{H^+} \cdot a_{HCO_3^-}}{a_{H_2CO_3}} \;, \qquad (3.35)$$

and

$$K_2 \;=\; \frac{a_{H^+} \cdot a_{HCO_3^-}}{a_{HCO_3^-}} \;. \qquad (3.36)$$

Also,

$$m_{CO_3} \;=\; c_{CO_3} \;+\; c_{HCO_3^-} \;+\; c_{H_2CO_3} \,. \qquad (3.37)$$

In Equation 3.37, m_{CO_3} is the total concentration of carbonate and is equal to the amount of sodium bicarbonate originally added. These three equations can be solved for $c_{HCO_3^-}$ and for $c_{CO_3^=}$, giving

$$c_{HCO_3^-} = \frac{m_{CO_3^=}}{1 + \frac{K_2 \cdot f_{HCO_3^-}}{a_{H^+} \cdot f_{CO_3^=}} + \frac{a_{H^+} \cdot f_{HCO_3^-}}{K_1}} \qquad (3.38)$$

and

$$c_{CO_3^=} = \frac{K_2 \cdot f_{HCO_3^-}}{a_{H^+} \cdot f_{CO_3^=}} \; c_{HCO_3^-} \quad . \qquad (3.39)$$

Further, the following equations are obvious:

$$c_{Na^+} = m_{CO_3^=} + m_{NaOH} \qquad (3.40)$$

$$c_{DH^-} = S - c_{DH_2} \qquad (3.41)$$

$$c_{OH^-} = \frac{K_w}{f_{OH^-} \cdot a_{H^+}} \qquad (3.42)$$

The activity coefficients were estimated from the second approximation to the Debye-Hückel equation (Equation 3.13, p. 64). The values of a_i used were taken from the data of Kielland (51), also given by Klotz (53); 4.5 X 10^{-8} for $CO_3^=$ and HCO_3^-, 6 x 10^{-8} for DH^-, and 3.5 X 10^{-8} for the OH^- ion. For the first approximation the ionic strength was taken as equal to that of the original buffer solution as reported by Bates and Bower (9).

The first and second dissociation constants of carbonic acid at 40.0°C. were taken directly or calculated from data in the literature. The values used were $K_1 = 5.05 \times 10^{-7}$, (40, 41, 56, 63), and $K_2 = 7.0 \times 10^{-11}$ (50, 56). The ion product of water at 40.0°C. was taken as $K_w = 2.919 \times 10^{-14}$ (8, 42).

The value of c_{DH_2} was obtained from the y intercept of a plot of solubility against $1/a_{H^+}$, according to Equation 3.34. It was found to be 0.00980 mole/l. for dimethylglyoxime, 0.09225 mole/l. for nioxime, and 0.06777 mole/l. for heptoxime.

The concentration of each ionic species was then calculated from Equations 3.38 through 3.42 and the second approximation to the ionic strength calculated.

$$\mu = 1/2(c_{Na^+} + c_{HCO_3^-} + 4\ c_{CO_3^=} + c_{DH^-} + c_{OH^-}) \quad (3.43)$$

For two of the most concentrated solutions a third approximation to the ionic strength was carried out. There was no significant improvement.

The ionization constant was then calculated from a plot of solubility against $1/(a_{H^+} f_{DH^-})$. According to Equation 3.34 the slope of this plot divided by c_{DH_2} is equal to the desired constant.

The graphs from which the constant was calculated are shown in Figures 12, 13, and 14, and in Table 27 some ionization constants measured at 25° and 40°C. are tabulated for comparison.

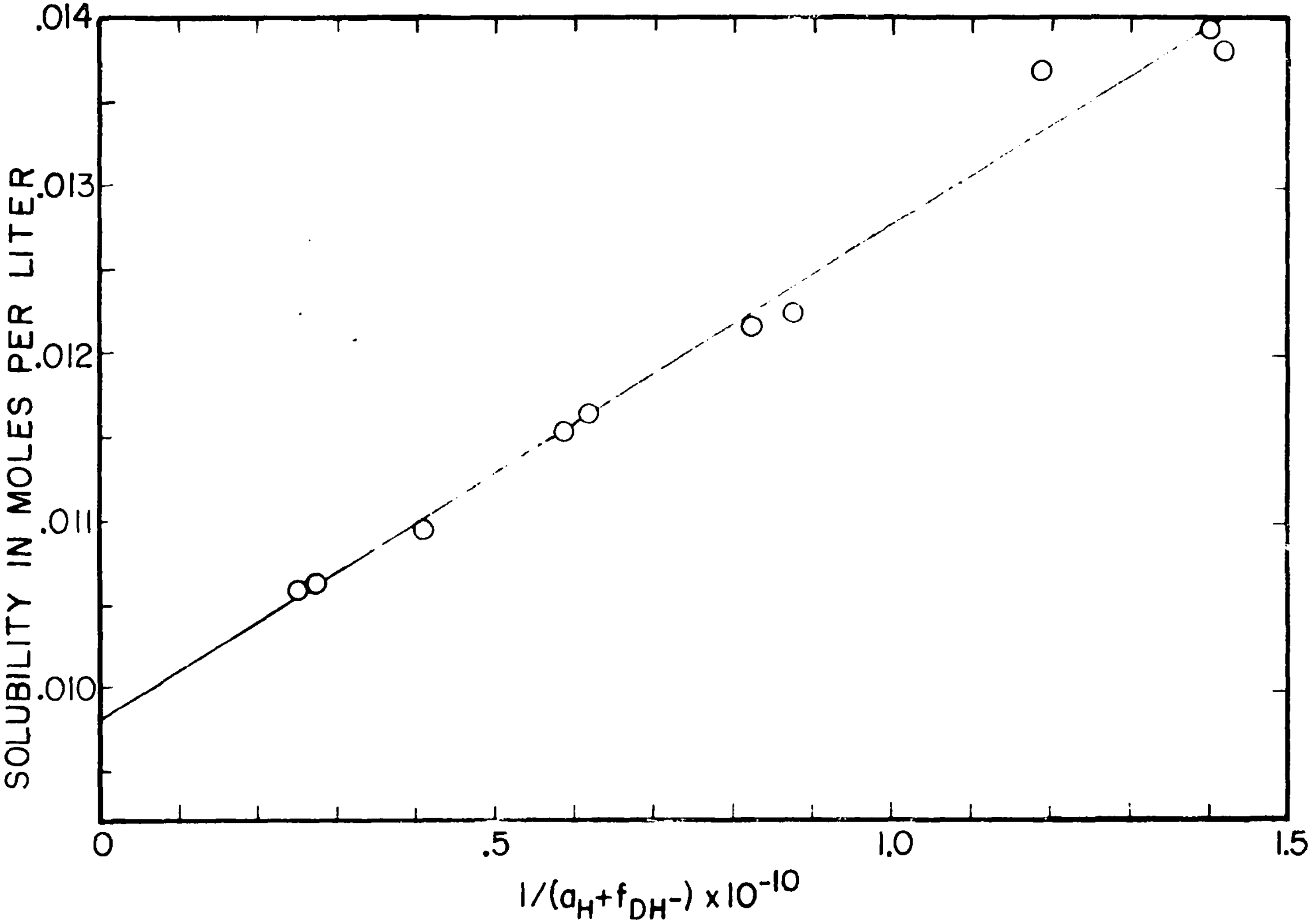


Figure 12. Graphical determination of the first ionization constant of dimethylglyoxime

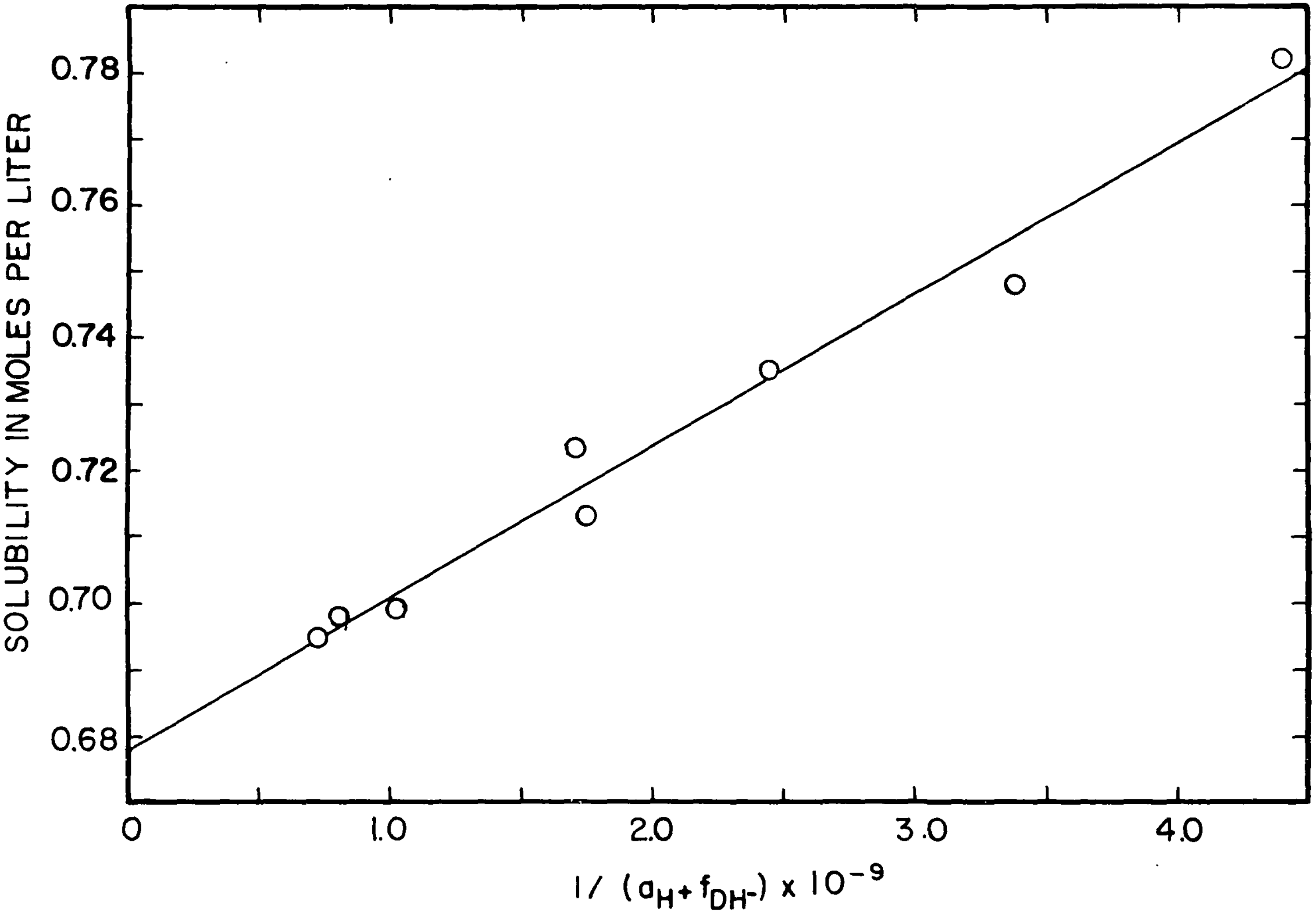


Figure 13. Graphical determination of the first ionization constant of nioxime

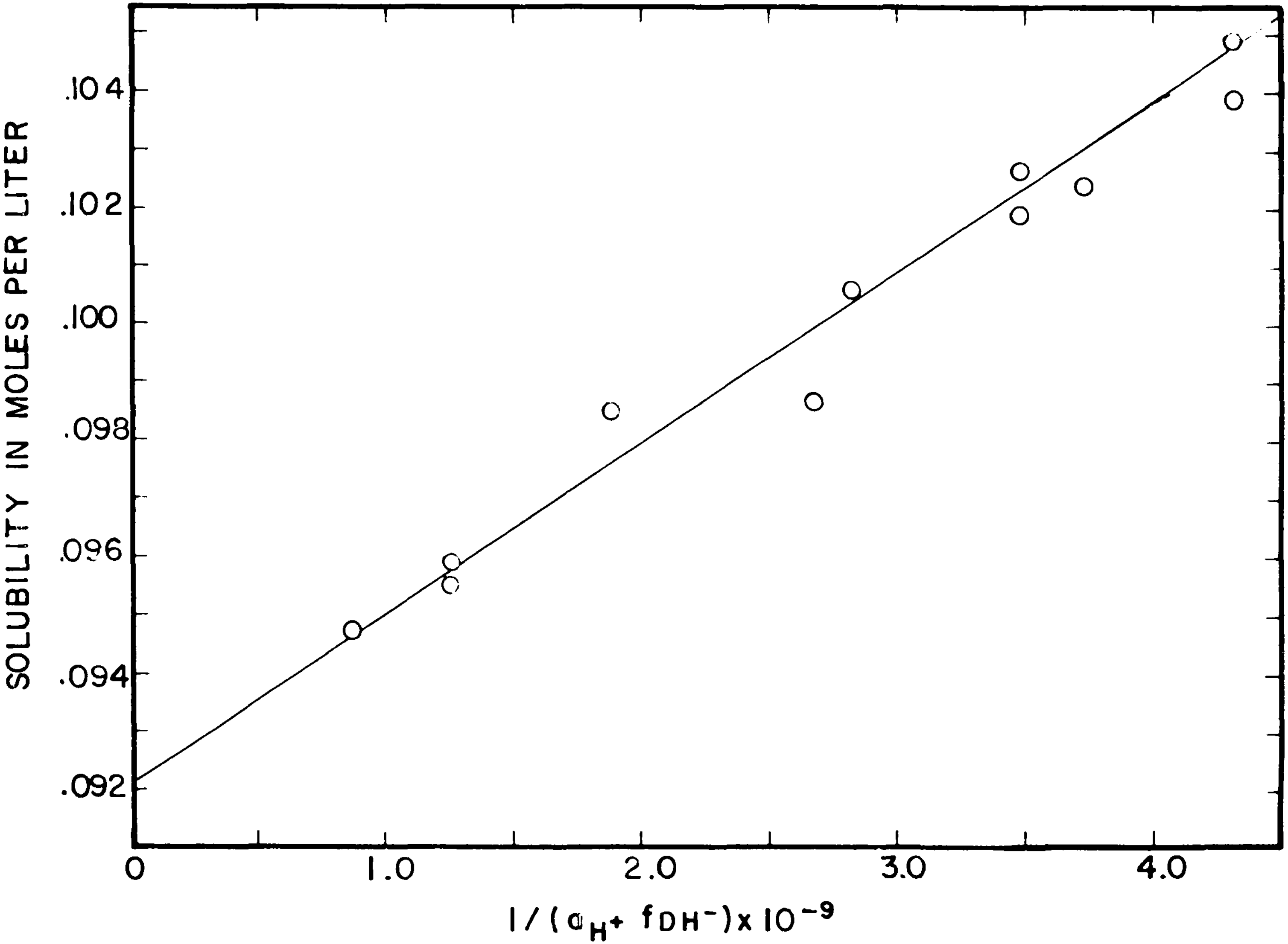


Figure 14. Graphical determination of the first ionization constant of heptoxime

Table 27. Acid dissociation constants of some *vic*-dioximes

vic-Dioxime	K_{DH_2} at 25°C.	K_{DH_2} at 40°C
dimethylglyoxime	2.5×10^{-11} [a]	3.0×10^{-11} [b]
	2.2×10^{-11} [c]	
	0.8×10^{-11} [d]	
nioxime	2.5×10^{-11} [a]	3.1×10^{-11} [b]
	4.0×10^{-11} [e]	
heptoxime	2.0×10^{-11} [d]	3.4×10^{-11} [b]

[a] (5)

[b] This work.

[c] (22)

[d] (3)

[e] (92)

IV. RESULTS AND DISCUSSION

A. Crystal Structure of vic-Dioxime Complexes

The majority of the nickel(II) and palladium(II) complexes have the same crystal structure as nickel dimethylglyoxime, which was determined by Godycki and Rundle (36), and is illustrated in Figures 1 and 2. The complexes that were studied are listed in Table 28 together with the metal-metal bond lengths, where they exist, and the position of the absorption band due to the metal-metal bonds. Each complex is marked with a superscript a, b, or c, indicating whether that complex has the same structure as nickel dimethylglyoxime, a slightly different structure containing metal-metal bonds, or an entirely different structure.

There are two notable cases of a different structure; palladium heptoxime, and nickel diaminoglyoxime.

Palladium heptoxime has a lower symmetry than nickel dimethylglyoxime, however, it crystallizes in long thin needles as the others do, and the absorption spectrum of the complex in colloidal suspension indicates the presence of -Pd-Pd- bonding. Comparison of the metal-metal bond lengths in Table 29 indicates that the bond in palladium heptoxime is unusually short. It is believed that adjacent molecules, for illustration in Figure 2, are no longer rotated exactly 90° with respect to each other, but through some smaller

Table 28. Crystal structure, metal-metal bond lengths, and position of absorption band due to metal-metal bonds in some *vic*-dioxime complexes of nickel and palladium

Complex	Metal-metal bond length	Position of -M-M- absorption
nickel 4-isopropylnioxime[a]	3.19	557
nickel dimethylglyoxime	3.233	554
nickel nioxime[a]	3.237	552
nickel 4-methylnioxime[a]	3.24	547
nickel 3-methylnioxime[a]	3.47	503
nickel α-furildioxime[a]	3.448	537
nickel α-benzildioxime[a]	3.547	515
nickel heptoxime[a]	3.596	465
nickel 4-*tert*-amylnioxime[b]	3.2	547
nickel diaminoglyoxime[c]	-	-
palladium nioxime[a]	3.250	482
palladium dimethylglyoxime[a]	3.253	480

---

[a] Complexes which have the same structure as nickel dimethylglyoxime.

[b] Complexes whose properties indicate the presence of metal-metal bonds but which have not been definitely shown to have the same crystal structure as nickel dimethylglyoxime.

[c] Complexes which have a different structure than nickel dimethylglyoxime.

Table 28. (Continued)

Complex	Metal-Metal bond length	Position of -M-M- absorption
palladium heptoxime[c]	3.329	425
palladium α-furildioxime[a]	3.459	460
palladium α-benzildioxime[a]	3.517	435

Table 29. Comparison of metal-metal bond lengths in some nickel and palladium complexes

Ligand	-Pd-Pd- bond length	-Ni-Ni- bond length
dimethylglyoxime	3.253	3.233
nioxime	3.250	3.237
α-furildioxime	3.459	3.448
α-benzildioxime	3.517	3.547
heptoxime	3.329	3.596

angle which allows a shorter -Pd-Pd- bond due to decreased steric hindrance and greater van der Waals attraction.

Nickel diaminoglyoxime has an entirely different crystal structure. The absorption spectrum of a single crystal using plane polarized light shows practically no dichroism, nor does the colloidal suspension exhibit a new absorption band in the visible region of the spectrum as complexes containing metal-metal bonds do. However, the lattice energy must be even lower than that of compounds which do contain metal-metal bonds, since it is insoluble not only in water but in a number of common organic solvents. The compound is soluble only in dimethylformamide and glacial acetic acid. The lattice constant along the c axis, the axis along which one would expect to find metal-metal bonds if they are present, is some multiple of 3.640 A.U. As will be shown later, metal-metal bonds of this length would be expected to contribute very little to the stability of the crystal. The insolubility of this complex is therefore due to some other factor.

The powder diffraction pattern of nickel 4-*tert*-amylnioxime made from the freshly prepared dioxime shows rather diffuse lines which generally agree with those of other complexes having the nickel dimethylglyoxime structure. Two years later the same batch of nickel complex gave the same diffuse diffraction pattern. However, freshly precipitated complex, using the *vic*-dioxime that had been prepared two years earlier, gave an entirely different diffraction pattern. The color of both complexes is about the same. No explanation for this behavior can be given.

B. Metal-Metal Bond Lengths

The metal-metal bond lengths measured in this work are reported in Table 28. One will notice that there is a very large spread, 3.2 to 3.6 A.U., between the shortest and the longest bonds. The covalent octahedral radius of Ni(II) is 1.39 A.U. (65). On this basis alone the length of a -Ni-Ni- bond would be on the order of 2.8 A.U. The fact that they are much longer indicates that these bonds are very weak. Rundle (73) has estimated that metal chains in nickel dimethylglyoxime contribute about 10 kcal./mole to the stability of the crystal, as opposed to about 60 kcal./mole for an average covalent bond.

One would expect that the length of the metal-metal bonds in a complex would depend to a large extent on the bulkiness of the vic-dioxime. The complexes nickel 4-isopropylnioxime and nickel 4-tert-amylnioxime appear to be exceptions since they both have shorter -Ni-Ni-bond lengths than nickel nioxime. However, Fisher-Hirschfelder-Taylor models of these two dioximes show that an isopropyl group or a tert-amyl group can be accomodated in the 4 position in two ways; one way would give rise to a great deal of steric hindrance to metal-metal bonds, and the other way would present little more hindrance than in nioxime itself. It appears that the complexes studied are in the later configuration and that the large alkyl substituents decrease the -Ni-Ni- bond length through increased van der Waals attraction rather than increasing it through steric hindrance.

C. Absorption Spectra of Single Crystals

The absorption spectra of single crystals of some nickel complexes are shown in Figures 15, 16, 17, 18, and 19. Plane polarized light was used. For each crystal the spectrum was measured with the plane of the polarized light parallel, $\parallel$, and perpendicular, $\perp$, to the plane of the molecules in the crystal. The intensity of absorption is unknown since the thicknesses of the crystals were not measured. However, the two orientations are comparable since the same crystal was used to obtain both curves.

In chlorofrom solution, nickel α-furildioxime and nickel α-benzildioxime have absorption bands at about 435 mμ and 406 mμ respectively, which are due to transitions within the molecule. Because of possible interference from these bands, these two complexes are not considered when comparing the dichroism with the metal-metal bond lengths.

In the case of nickel dimethylglyoxime, nickel nioxime, and nickel heptoxime, the effect of the length of the metal-metal bond on the dichroism is readily apparent. Nickel

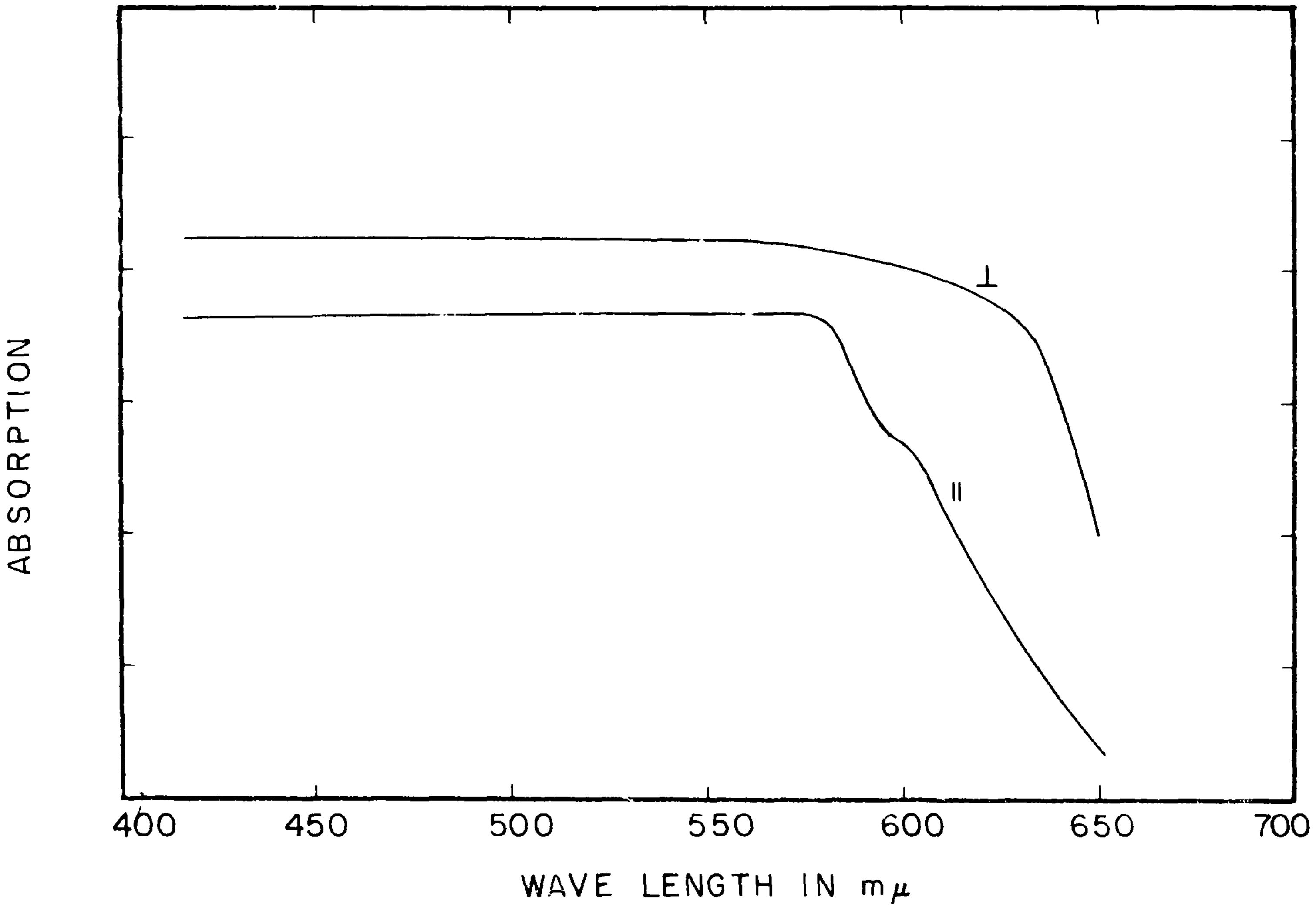


Figure 15. Absorption spectrum of a single crystal of nickel dimethylglyoxime

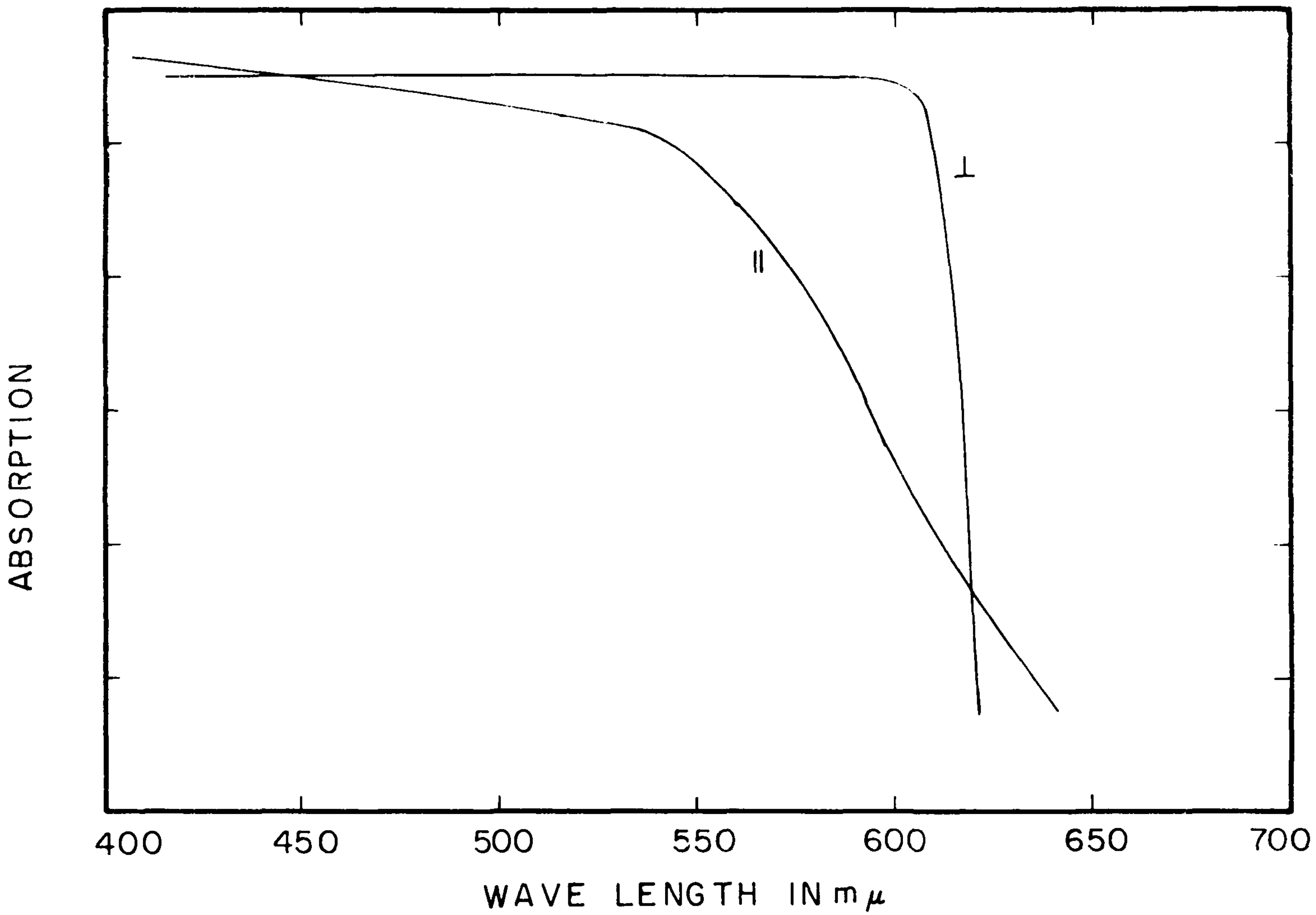


Figure 16. Absorption spectrum of a single crystal of nickel nioxime

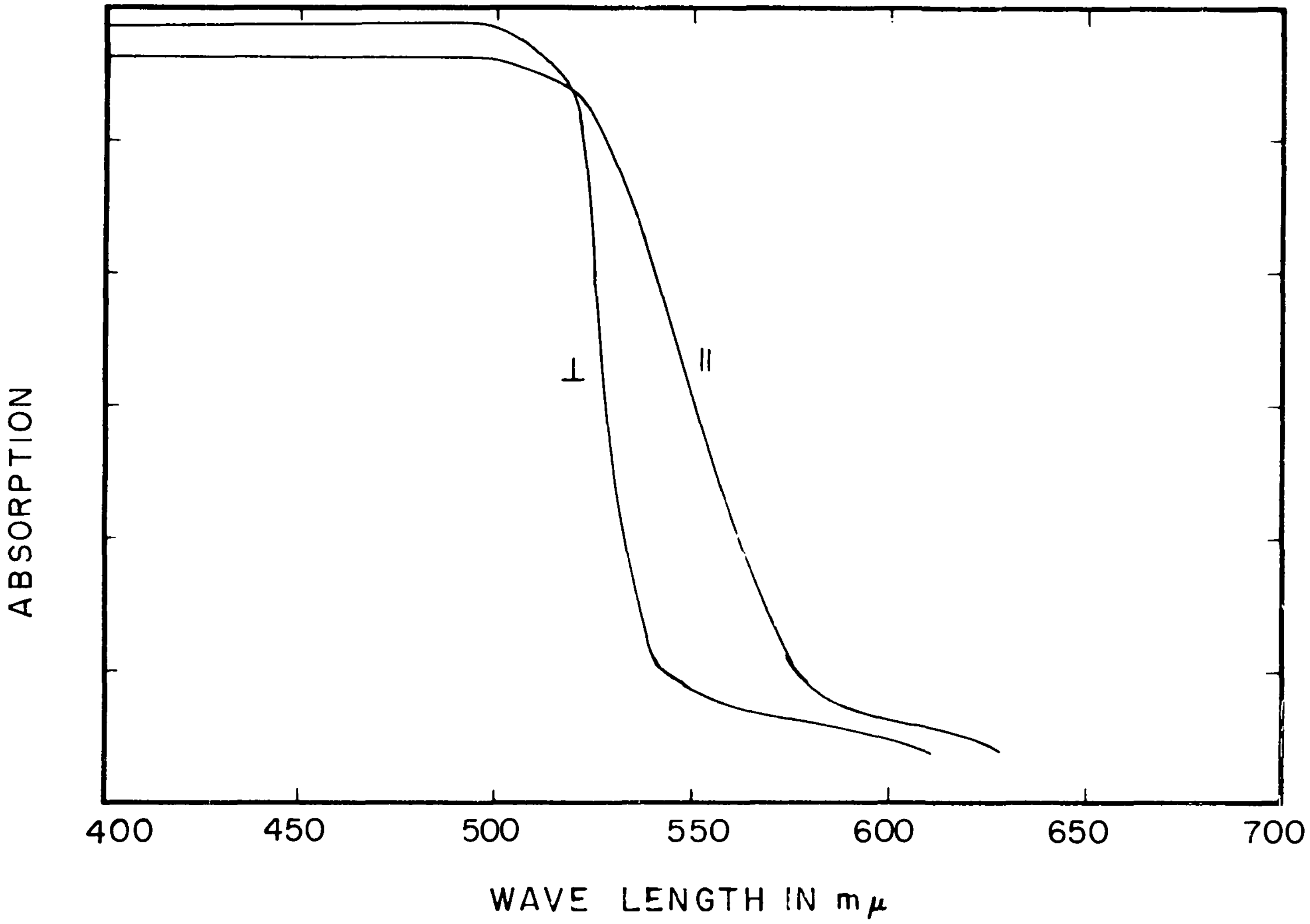


Figure 17. Absorption spectrum of a single crystal of nickel heptoxime

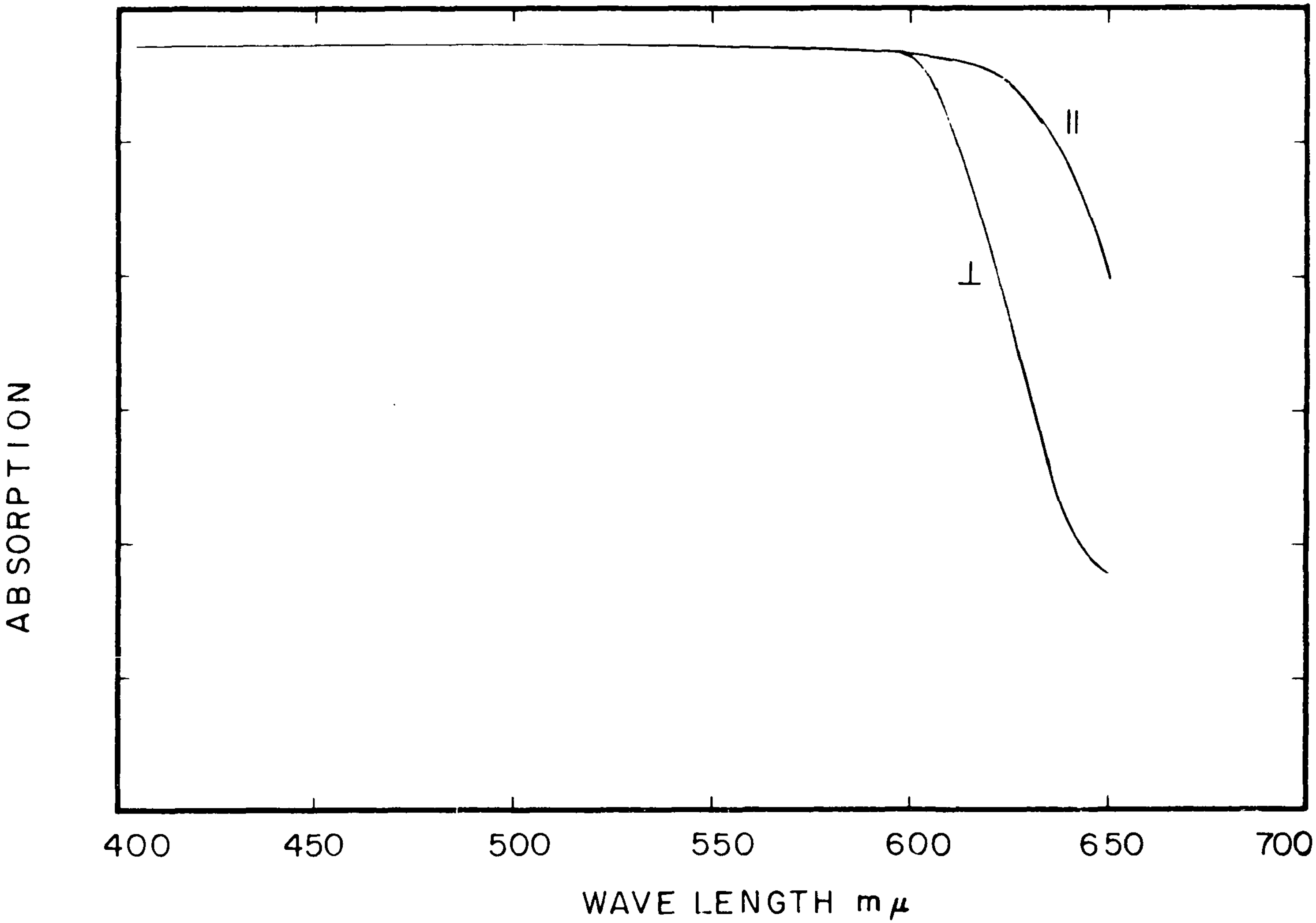


Figure 18. Absorption spectrum of a single crystal of nickel α-furildioxime

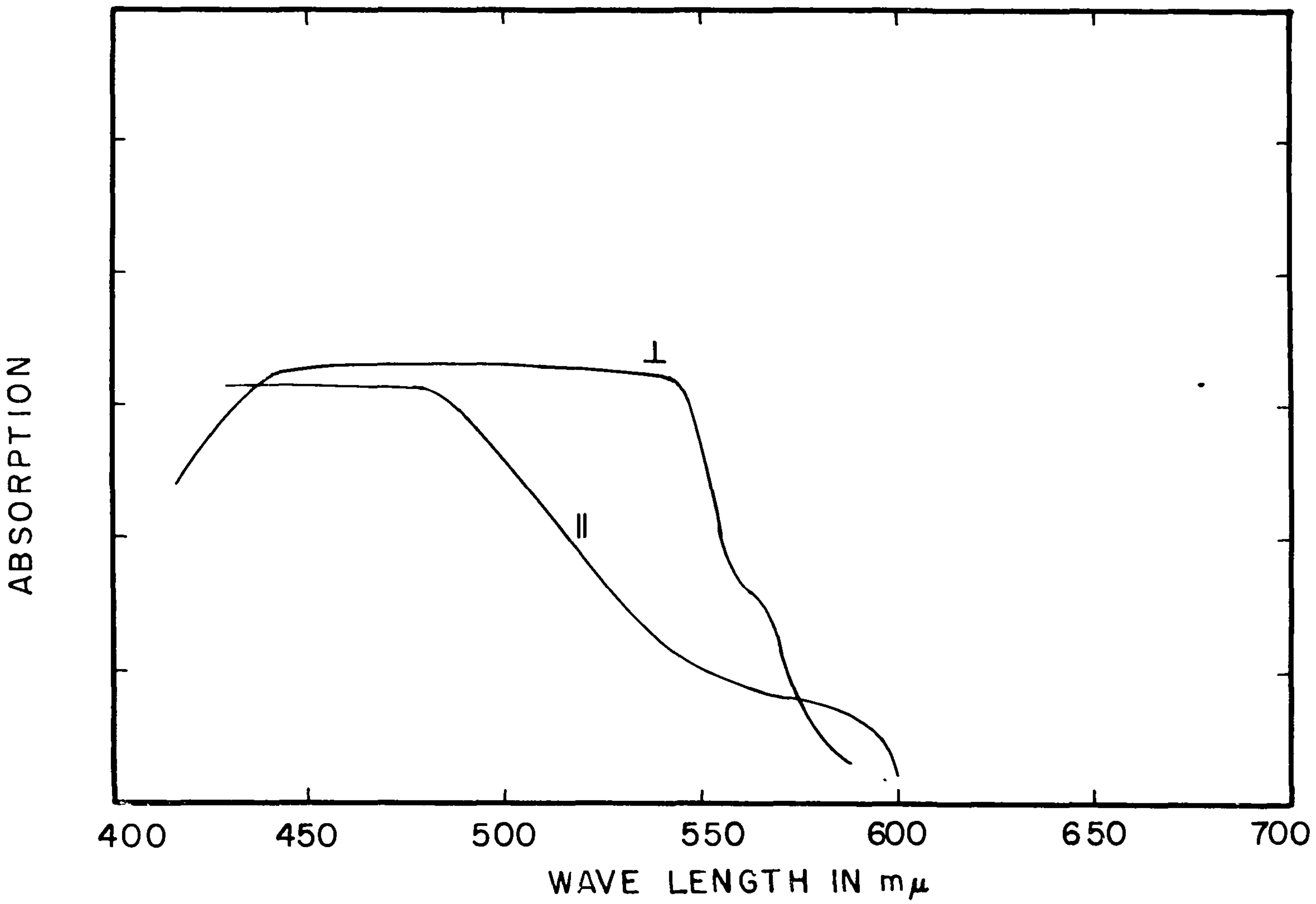


Figure 19. Absorption spectrum of a single crystal of nickel α-benzildioxime

dimethylglyoxime and nickel nioxime, which have almost identically the same nickel-nickel bond lengths, also show dichroism of about equal intensity. Furthermore, since these are among the shortest nickel-nickel bonds, and therefore the strongest, dichroism is much stronger than in nickel heptoxime, which has a very long nickel-nickel bond. In fact, the dichroism in nickel heptoxime has practically reverted to the "normal" situation where maximum absorption occurs when the plane of the polarized light is parallel to the molecules. Indeed, the spectra of nickel heptoxime indicate that there is very little metal-metal interaction. It should also be noticed that the absorption occurs at much lower wavelengths for nickel heptoxime. A similar shift in this absorption band with metal-metal bond length is described in the section on the absorption of light by colloidal suspensions of these compounds.

The dichroism of nickel α-benzildioxime indicates the presence of appreciable metal-metal bonding, while that of nickel α-furildioxime does not. This is believed to be due to interference from the nearby absorption band in nickel-α-furildioxime already mentioned, while in nickel α-benzildioxime this band is apparently far enough away that it does not interfere.

The dichroic properties of crystals of several nickel and palladium complexes of *vic*-dioximes are shown in Table 30. The colors were observed through a polarizing microscope.

Table 30. Dichroism of some nickel and palladium complexes containing metal-metal bonds

Complex	-M-M- bond length	Orientation of plane polarized light	
		∥	⊥
nickel dimethylglyoxime	3.233	red	dark red
nickel nioxime	3.237	red	dark red
nickel α-furildioxime	3.448	very dark red	dark red
nickel α-benzildioxime	3.547	yellow	orange
nickel heptoxime	3.596	orange	yellow
palladium dimethylglyoxime	3.253	yellow	red
palladium nioxime	3.250	orange	red
palladium α-furildioxime	3.459	red	orange
palladium α-benzildioxime	3.517	dark yellow	yellow
palladium heptoxime	3.329	light yellow	yellow

It will be noticed that with the plane of polarized light vibrating perpendicular to the plane of the molecules, that is, parallel to the metal chains, the color changes from red, through orange, to yellow as the metal-metal distance increases. The effect of metal-metal bond length on the color will be discussed in more detail presently.

One can also see in Table 30 that the visually observed colors agree with the absorption spectra. The nickel and palladium complexes of dimethylglyoxime and nioxime clearly absorb more blue light when the plane of polarized light is perpendicular to the molecules than when it is parallel. Nickel heptoxime, which has a very weak -Ni-Ni- bond shows the opposite effect. Thus, simple observation of the dichroism of these complexes can lead to useful information about the presence and strength of metal-metal bonding, provided the *vic*-dioxime is not conjugated with another group.

D. Absorption Spectra of Colloidal Suspensions

In Figures 20 through 29, the absorption spectra of colloidal suspensions of several nickel and palladium complexes which contain metal-metal bonds are compared with the spectra of their chloroform solutions. In nearly every case one sees that the colloidal suspension has an absorption band in the region of 425 mμ to 557 mμ that is not

Figure 20. Comparison of absorption spectra of chloroform solution and colloidal suspension of nickel dimethylglyoxime

Curve 1, chloroform solution;

Curve 2, colloidal suspension.

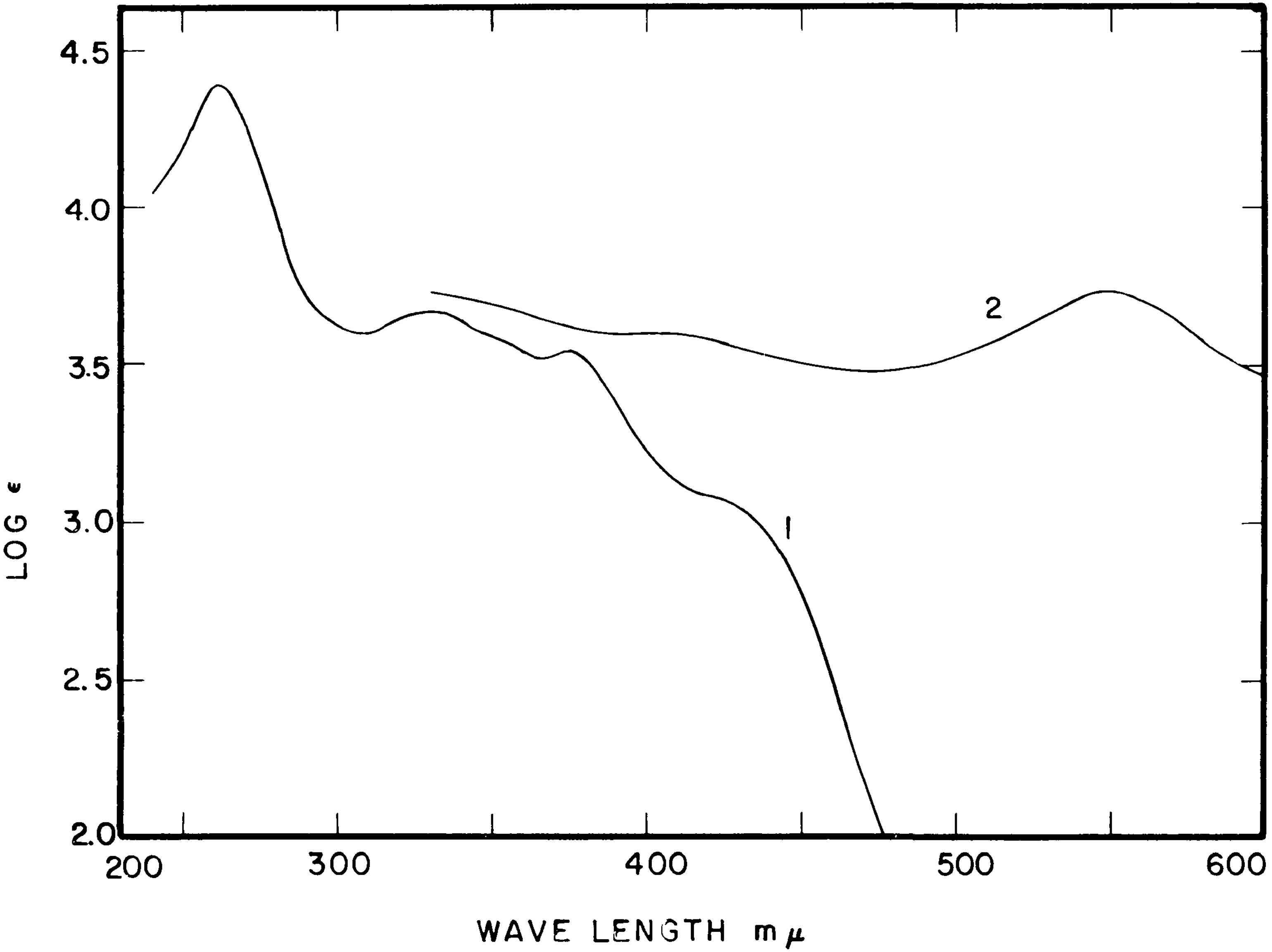

4.5
4.0
3.5
3.0
2.5
2.0
LOG ϵ
200
300
400
500
600
WAVE LENGTH mμ
1
2

Figure 21. Comparison of absorption spectra of chloroform solution and colloidal suspension of nickel nioxime

Curve 1, chloroform solution;

Curve 2, colloidal suspension.

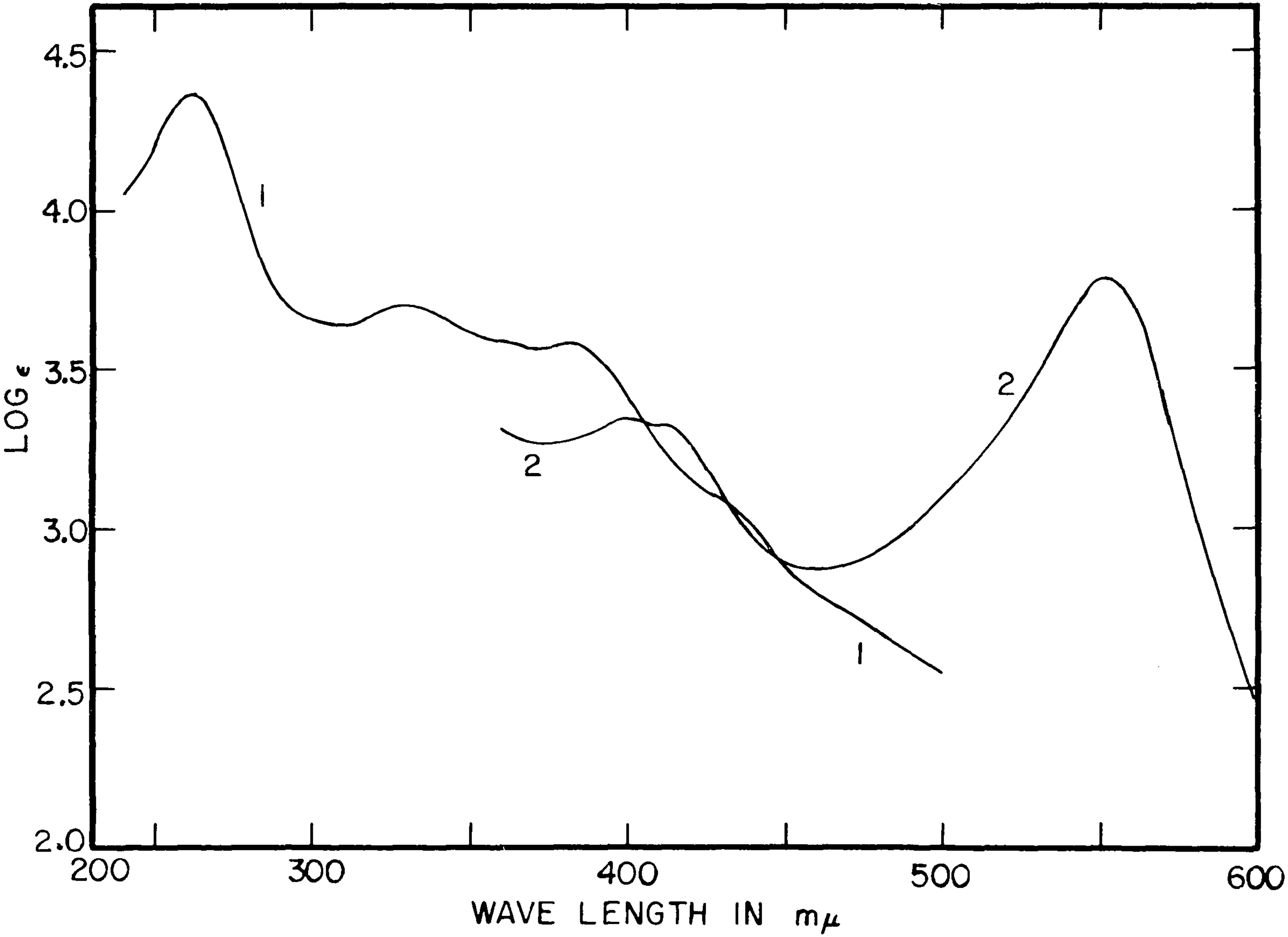

4.5
4.0
3.5
3.0
2.5
2.0
LOG ε
200
300
400
500
600
WAVE LENGTH IN mμ
1
1
2
2

Figure 22. Comparison of absorption spectra of chloroform solution and colloidal suspension of nickel α-furildioxime

Curve 1, chloroform solution;

Curve 2, colloidal suspension.

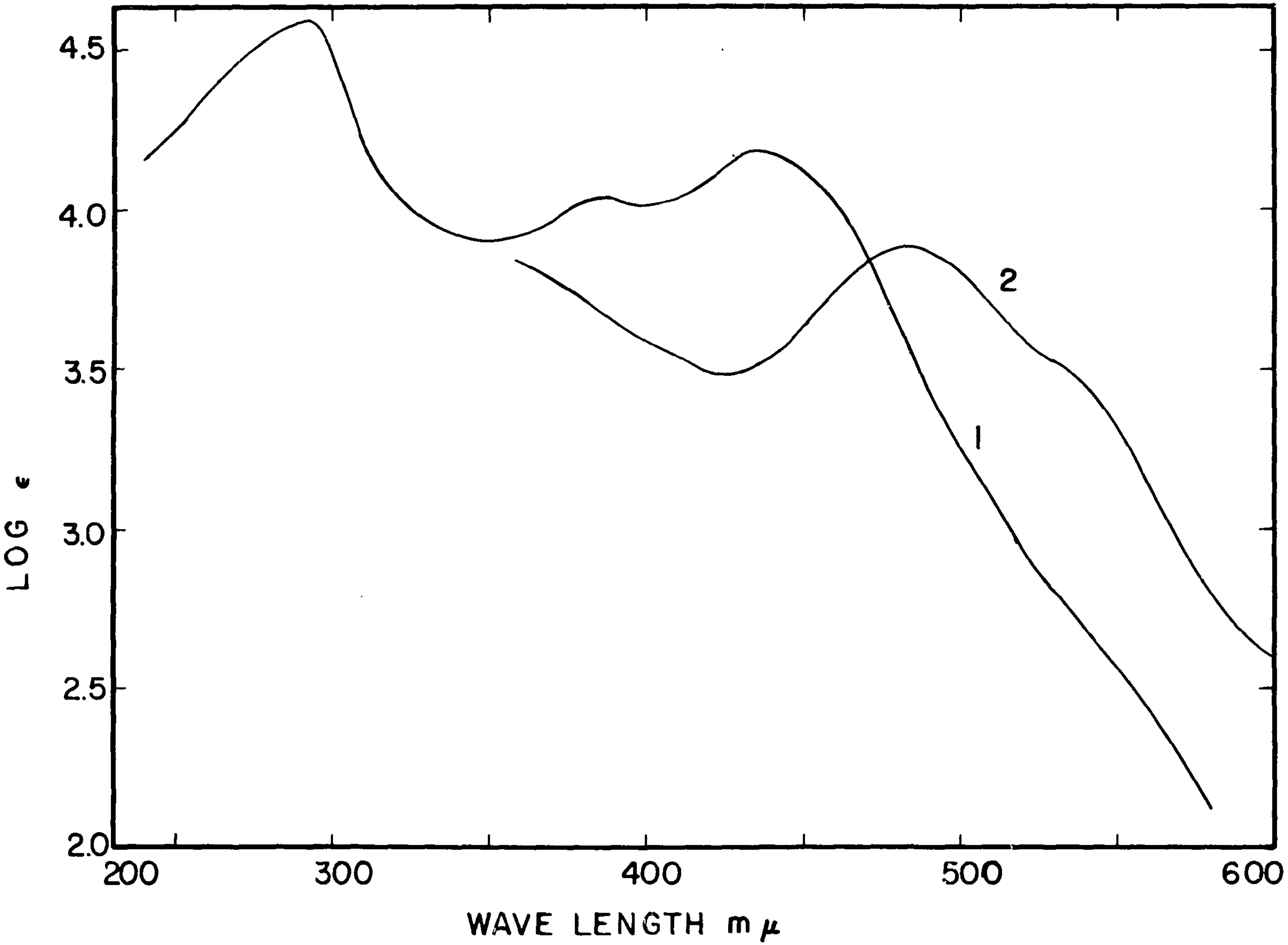

4.5
4.0
3.5
3.0
2.5
2.0
LOG ε
200
300
400
500
600
WAVE LENGTH mμ
1
2

Figure 23. Comparison of absorption spectra of chloroform solution and colloidal suspension of nickel α-benzildioxime

Curve 1, chloroform solution;

Curve 2, colloidal suspension.

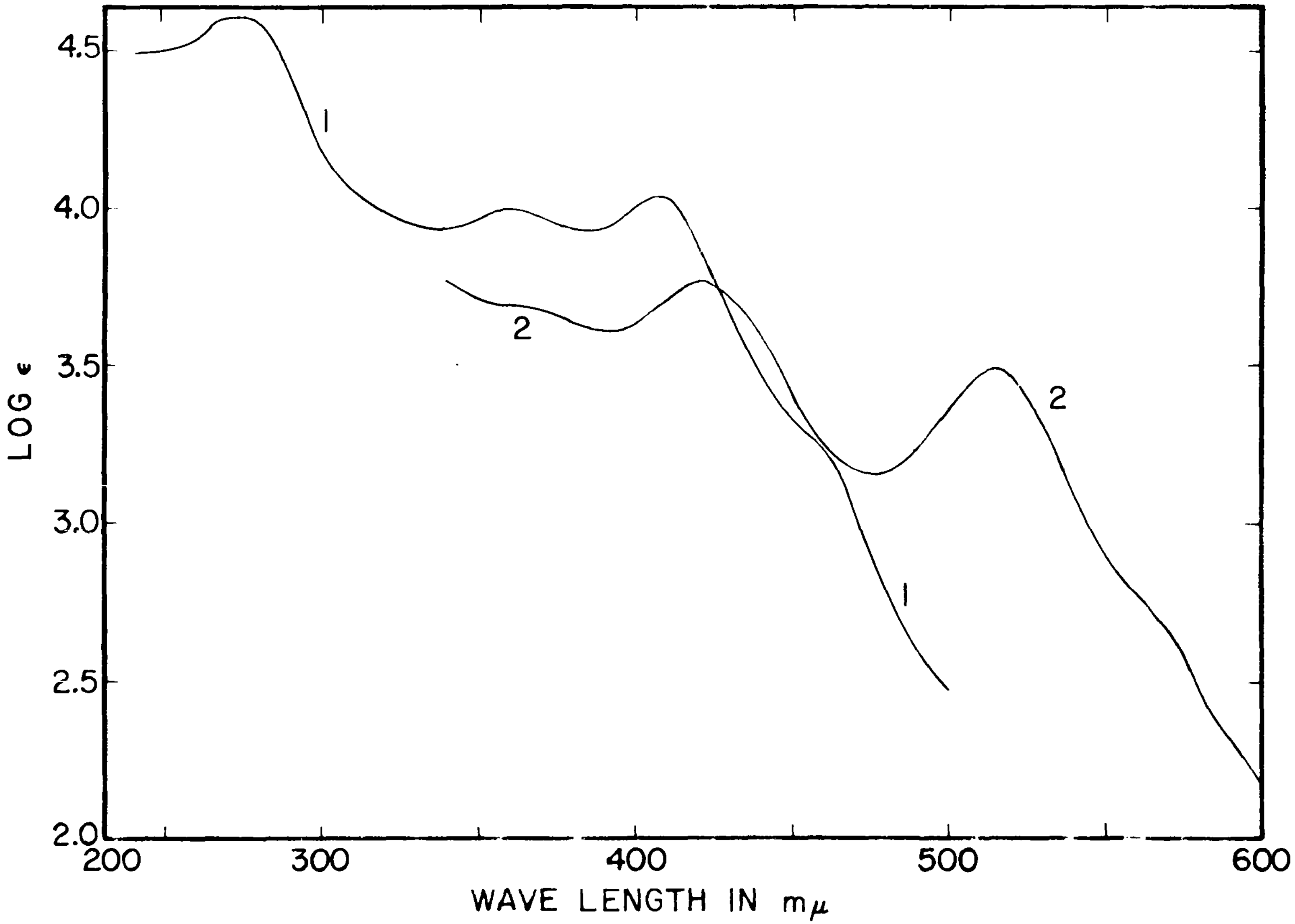

4.5
4.0
3.5
3.0
2.5
2.0
LOG ε
200
300
400
500
600
WAVE LENGTH IN mμ
1
1
2
2

Figure 24. Comparison of absorption spectra of chloroform solution and colloidal suspension of nickel heptoxime

Curve 1, chloroform solution;

Curve 2, colloidal suspension.

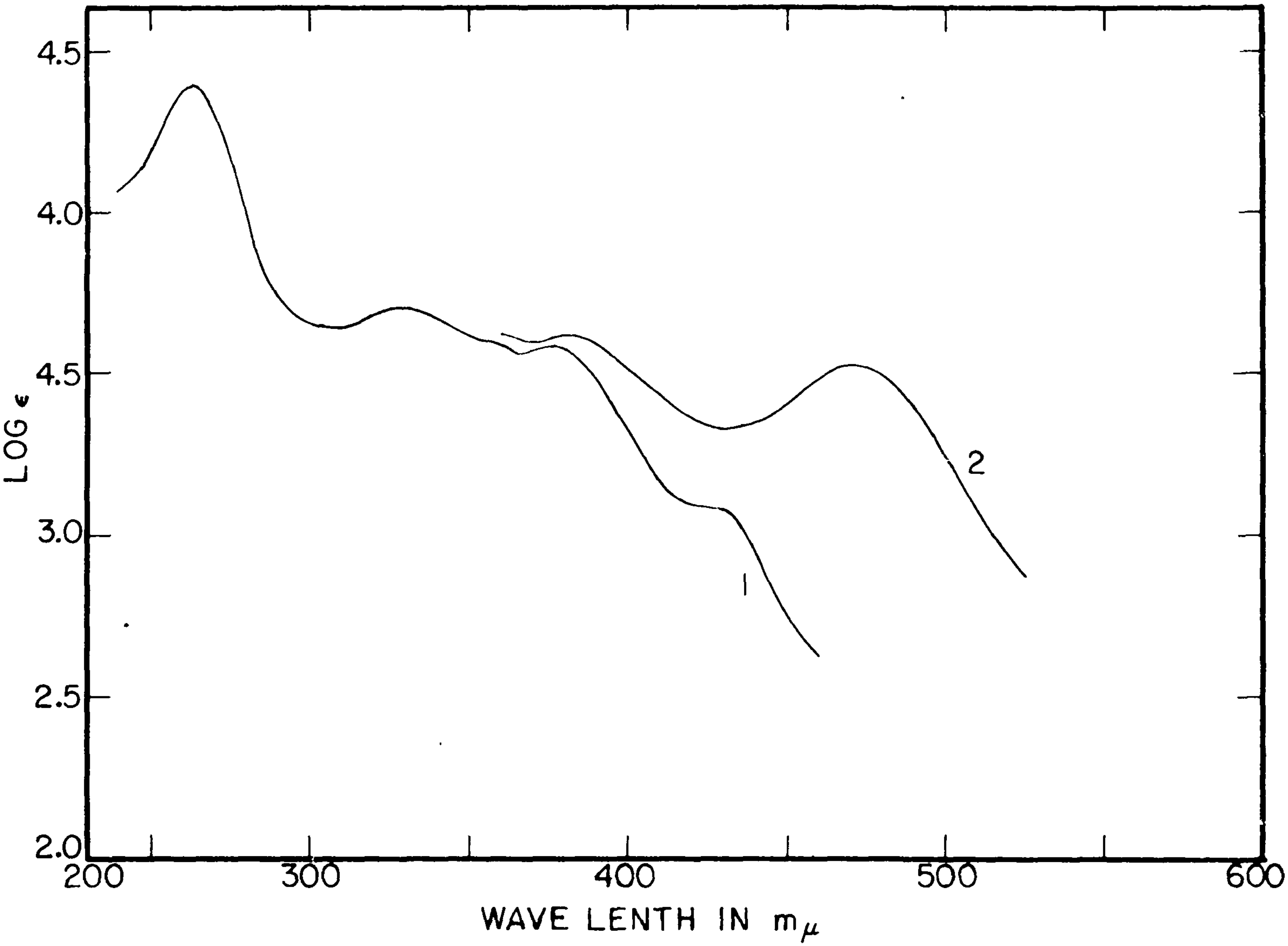

4.5
4.0
4.5
3.0
2.5
2.0
LOG ε
200
300
400
500
600
WAVE LENTH IN mμ
1
2

Figure 25. Comparison of absorption spectra of chloroform solution and colloidal suspension of palladium nioxime

Curve 1, chloroform solution;

Curve 2, colloidal suspension.

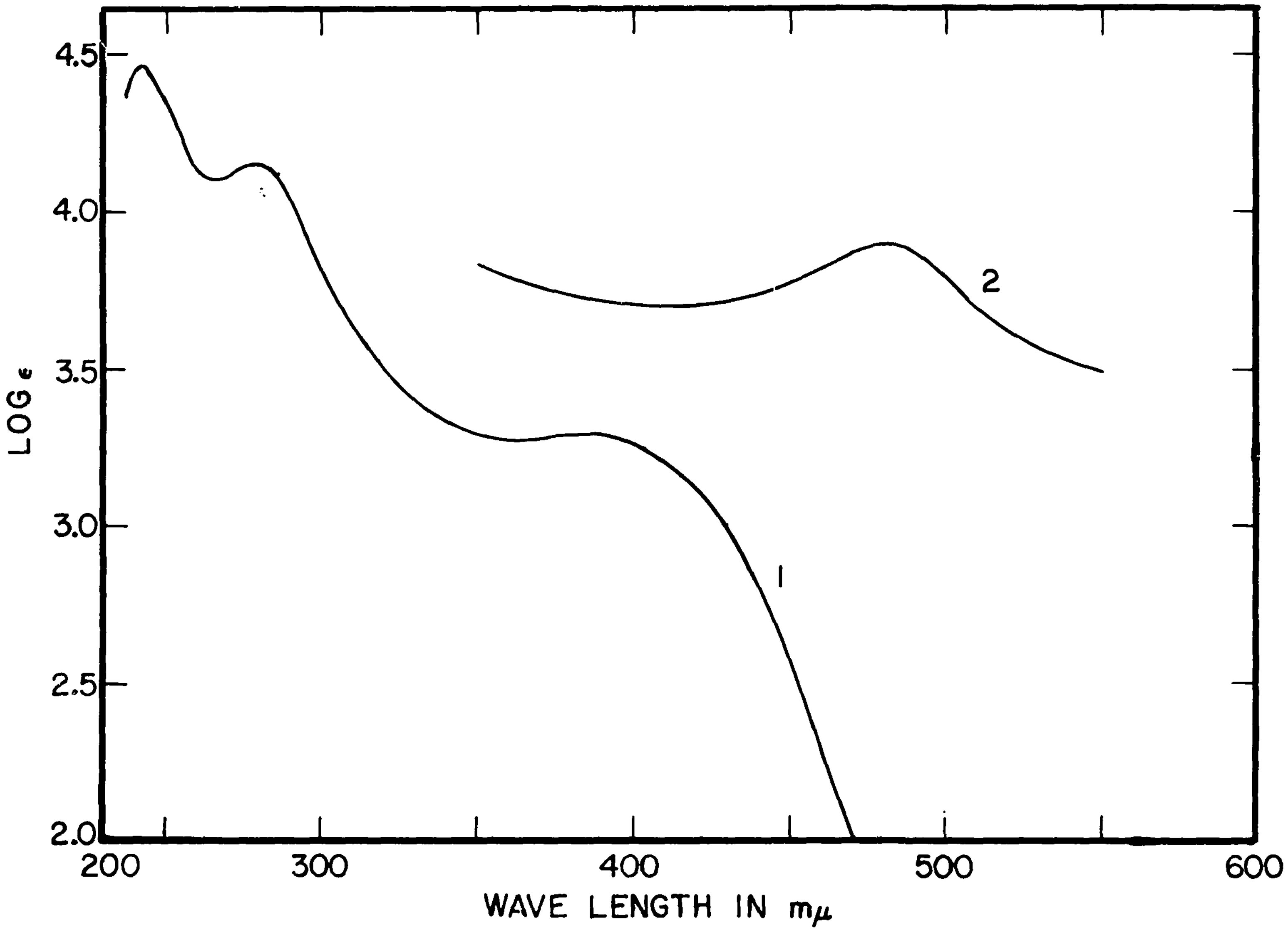

4.5
4.0
3.5
3.0
2.5
2.0
LOG ε
200
300
400
500
600
WAVE LENGTH IN mμ
1
2

Figure 26. Comparison of absorption spectra of chloroform solution and colloidal suspension of palladium dimethylglyoxime

Curve 1, chloroform solution;

Curve 2, colloidal suspension.

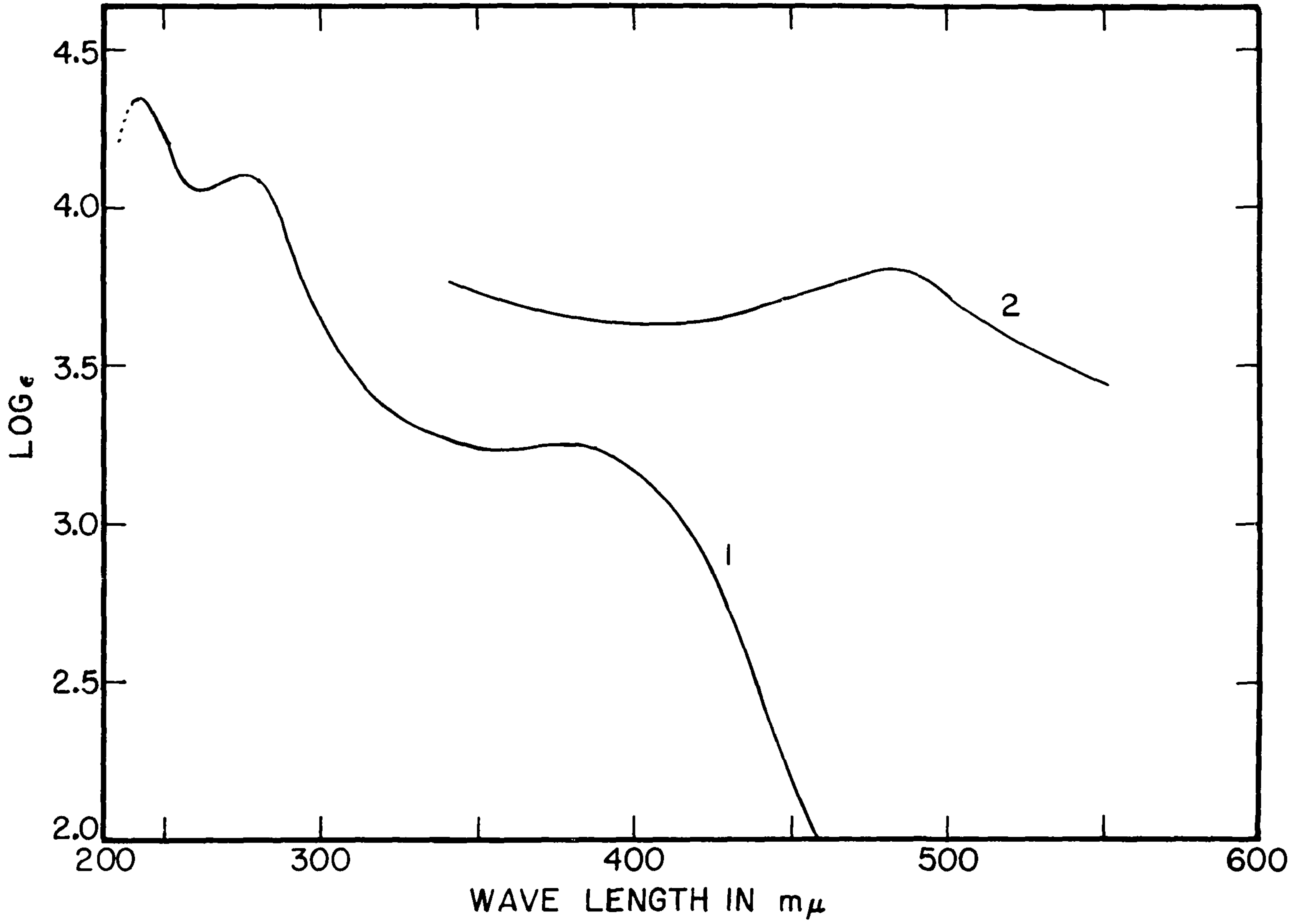

4.5
4.0
3.5
3.0
2.5
2.0
LOG ε
200
300
400
500
600
WAVE LENGTH IN mμ
1
2

Figure 27. Comparison of absorption spectra of chloroform solution and colloidal suspension of palladium heptoxime

Curve 1, chloroform solution;

Curve 2, colloidal suspension.

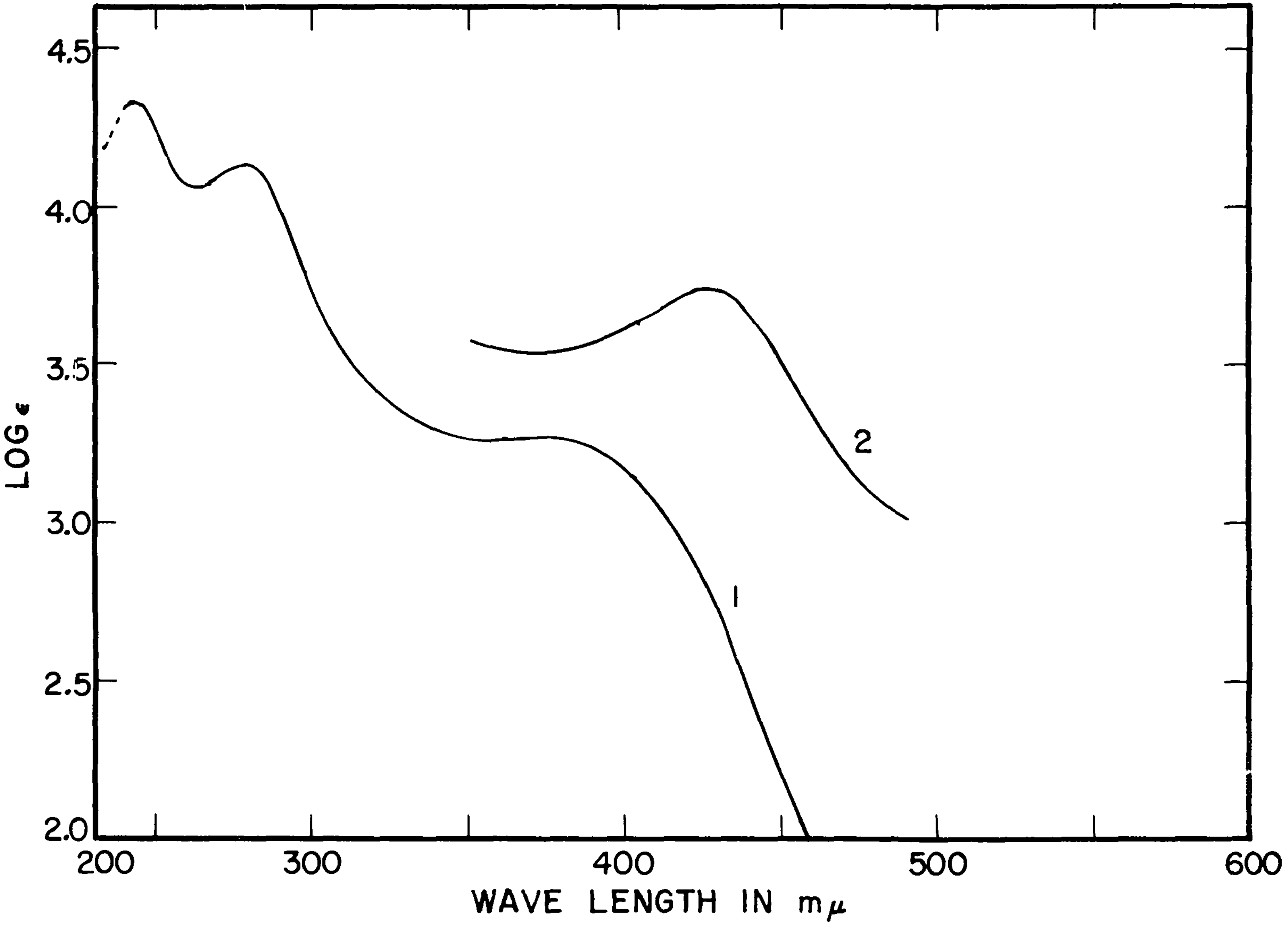

4.5
4.0
3.5
3.0
2.5
2.0
LOG ε
200
300
400
500
600
WAVE LENGTH IN mμ
1
2

Figure 28. Comparison of absorption spectra of chloroform solution and colloidal suspension of palladium α-furildioxime

Curve 1, chloroform solution;

Curve 2, colloidal suspension.

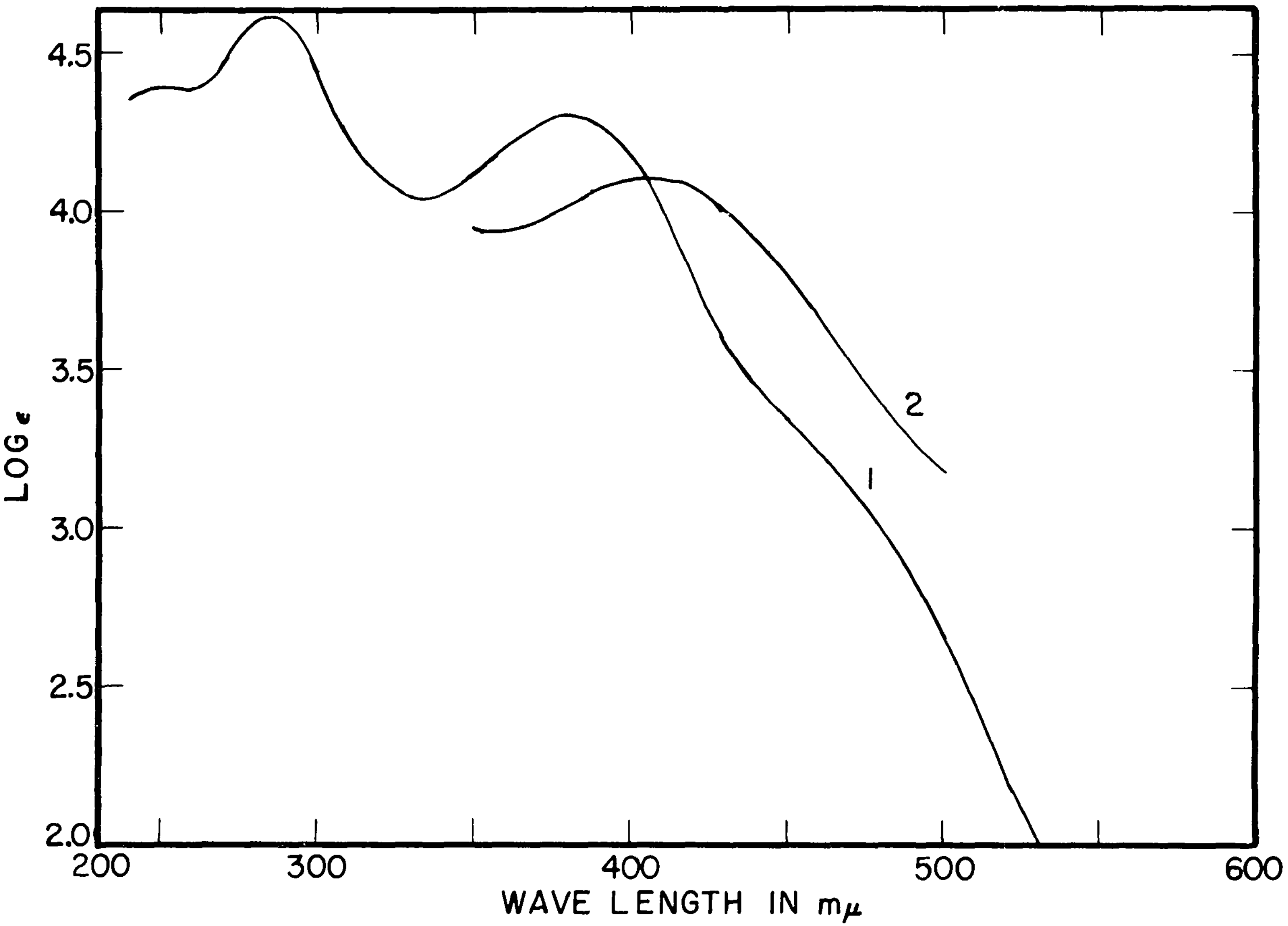
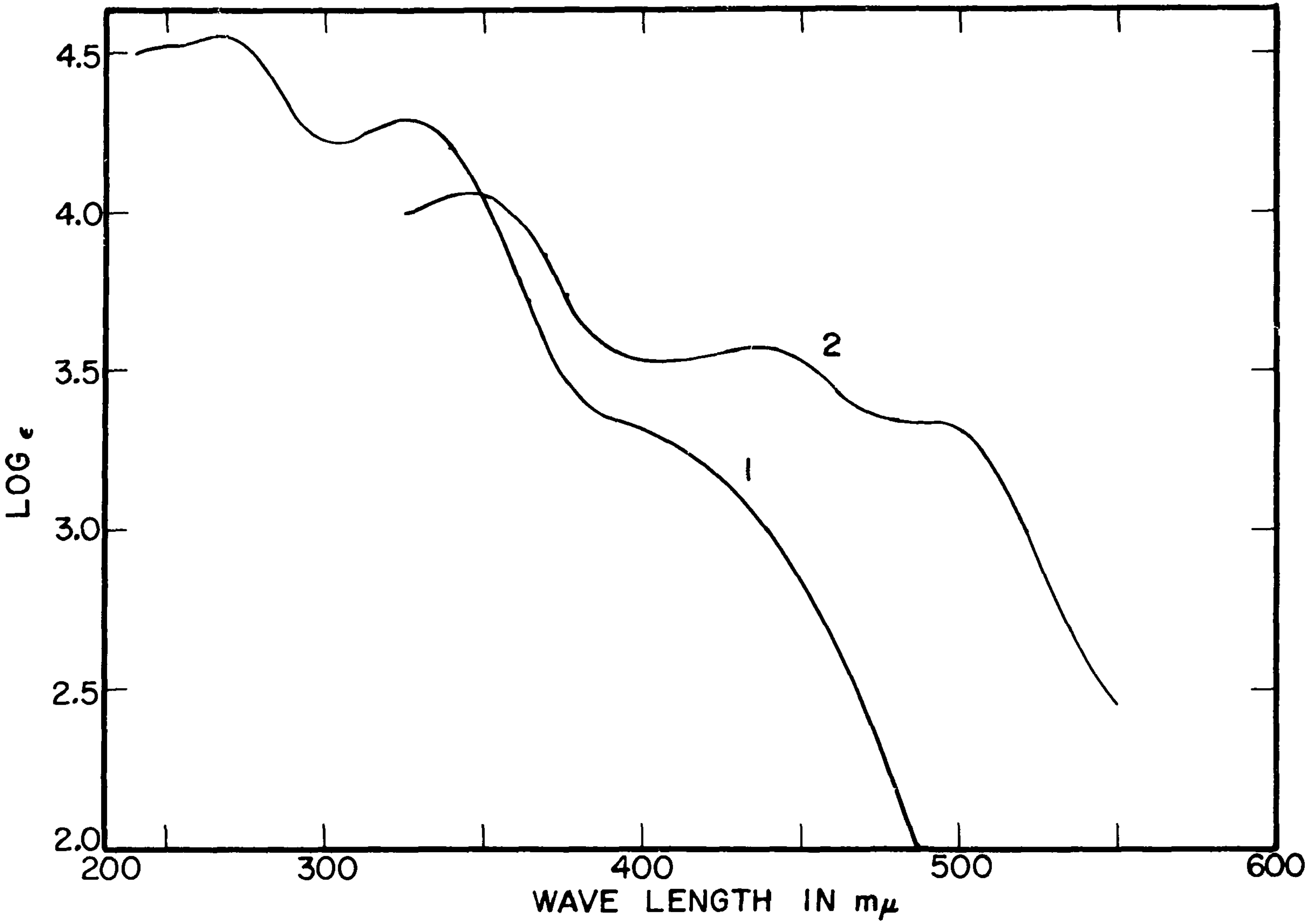

4.5
4.0
3.5
3.0
2.5
2.0
LOG ε
200
300
400
500
600
WAVE LENGTH IN mμ
1
2

Figure 29. Comparison of absorption spectra of chloroform solution and colloidal suspension of palladium α-benzildioxime

Curve 1, chloroform solution;

Curve 2, colloidal suspension.


LOG ε
4.5
4.0
3.5
3.0
2.5
2.0
200
300
400
500
600
WAVE LENGTH IN mμ
1
2

present in the spectrum of the molecule in solution. The appearance of a new absorption band requires some disturbance of the electronic structure, which in this case must be due to the formation of metal-metal bonds.

The absorption spectra of the pulverized solids pressed into KBr pellets were also measured in the visible region. In most cases these were very close to the spectrum of the colloidal suspensions, although the bands were somewhat broader. In some cases the bands were so broad that no definite maximum could be located, and in other cases the signal to noise ratio of the spectrophotometer became so low that determination of the spectrum was impossible.

The positions of maximum absorption of the bands due to metal-metal bonding are given in Table 28. For most complexes the position of this band is readily apparent. However, in the cases of nickel α-furildioxime and palladium α-furildioxime the desired band is obscured by a more intense band which is found in chloroform solutions as well as in the colloidal suspensions. In order to locate the metal-metal absorption band it was necessary to resolve the total absorption curve into its component bands. This was done by the method of Lowry and Hudson (55) and of Jørgensen (48). In this procedure an absorption band is treated as a Gaussian distribution described by the equation

$$\log \epsilon_o = \log \epsilon + \left[\frac{\lambda - \lambda_o}{\beta}\right]^2 \qquad (4.1)$$

in which λ_o and ϵ_o are the wavelength and molar absorptivity of an individual band at the position of maximum absorption, and β is a parameter which determines the half width of the band. The value of β may be different for the long wavelength and the short wavelength side of a band, in which case it is designated as β_+ and β_-, respectively.

The method of resolving the total absorption into its component bands is one of trial and error in which values of λ_o, ϵ_o, and β are guessed at until the sum of the individual bands gives the observed absorption spectrum within reasonable limits.

The case of nickel α-furildioxime is shown in Figure 30. The two bands which were obtained have the following parameters: $\lambda_o = 482$ mμ, $\epsilon_o = 9950$, and $\beta = 49$ for one band, and $\lambda_o = 537$ mμ, $\epsilon_o = 3650$, and $\beta = 40$ for the band due to nickel-nickel bonding. For both of these bands $\beta_+ = \beta_-$.

The absorption spectrum of palladium α-furildioxime was also resolved into its component bands. In this case it was necessary to postulate three bands in order to obtain the observed spectrum. The result, is shown in Figure 31, and the parameters of the three bands are: $\lambda_o = 387$ mμ, $\epsilon_o = 9950$, $\beta = 43$; $\lambda_o = 422$ mμ, $\epsilon_o = 8800$, $\beta_+ = 42$,

Figure 30. Resolution of the spectrum of nickel α-furildioxime in colloidal suspension into its component bands

Solid line is the observed spectrum;

Dashed lines are individual absorption bands;

Circles represent the sum of the individual bands.

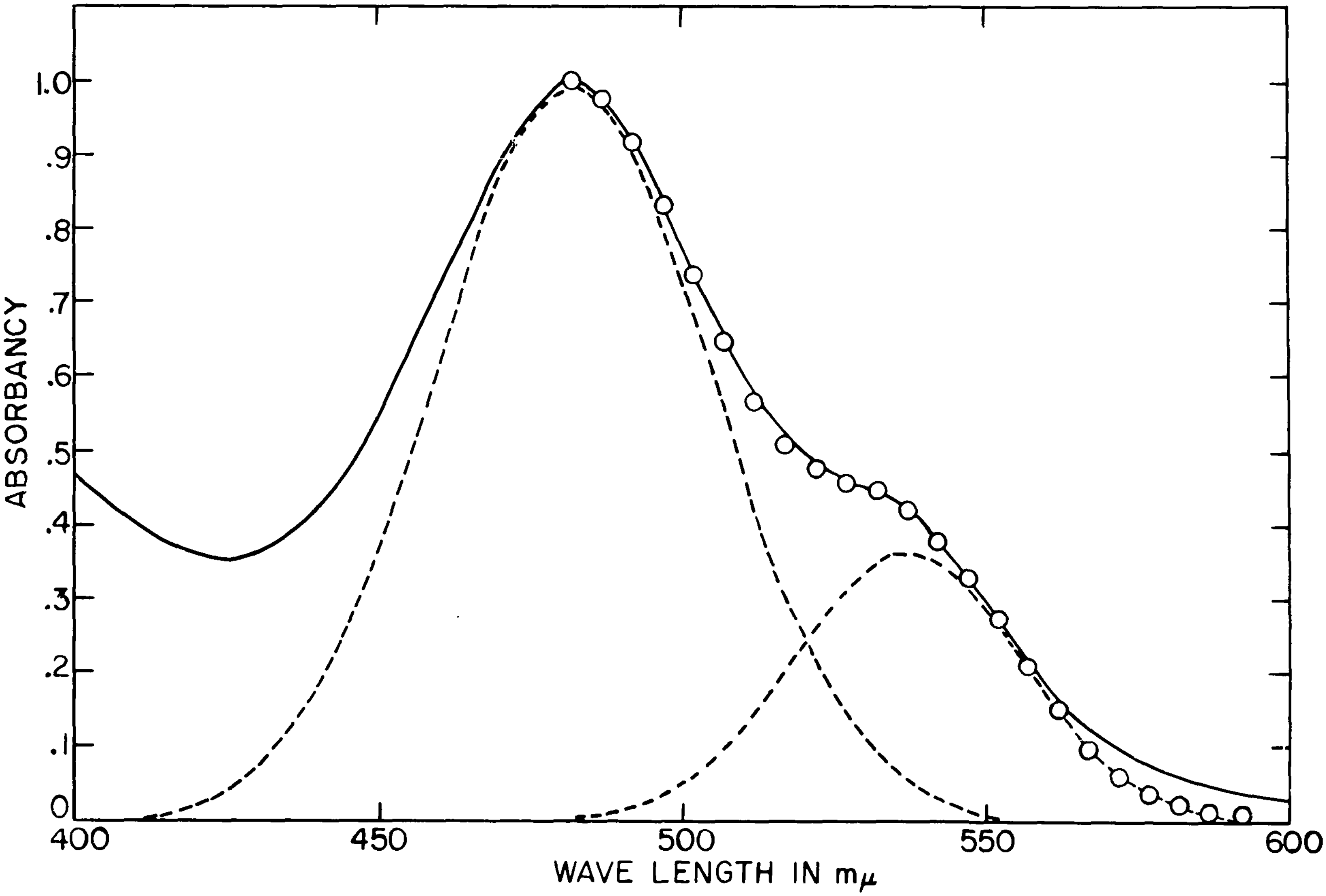
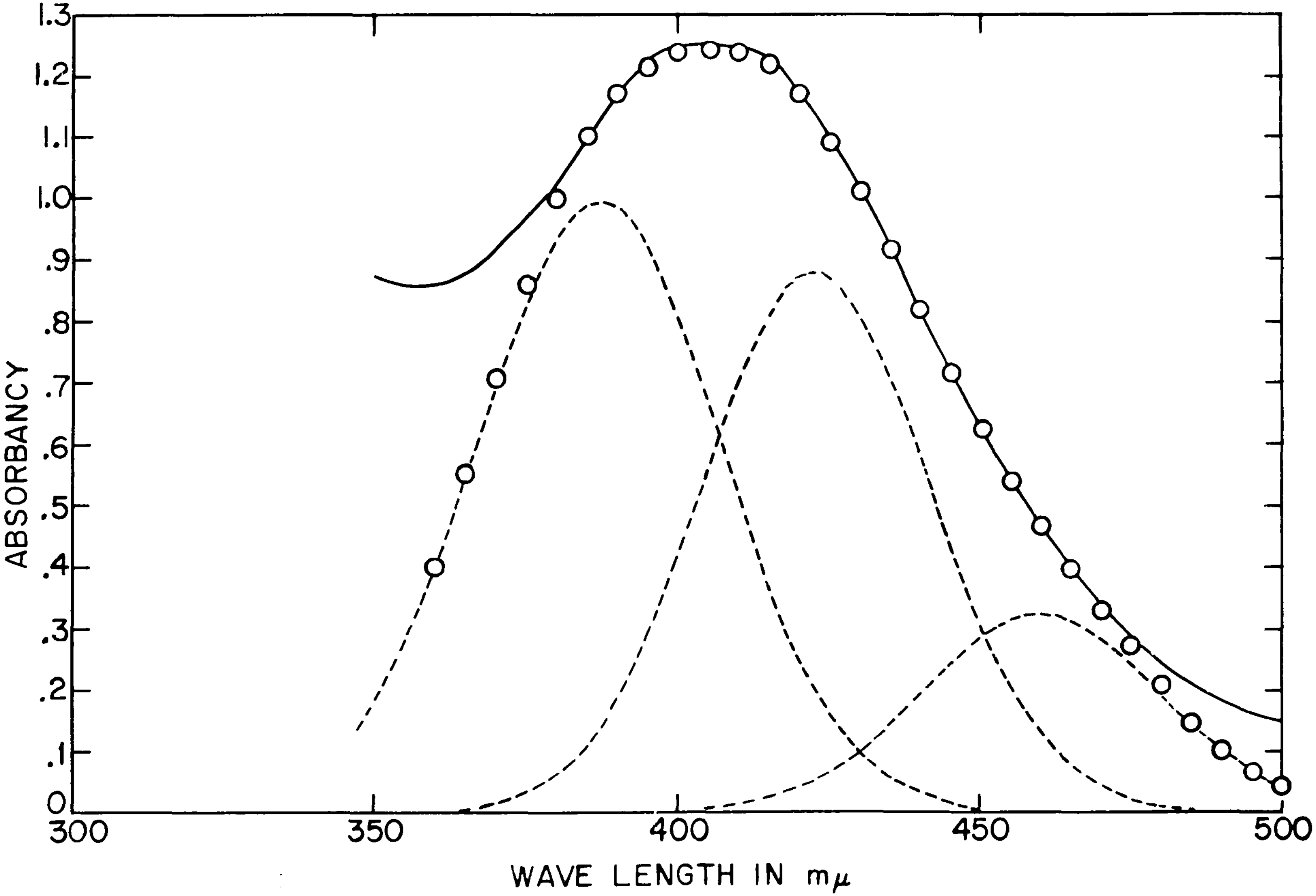

ABSORBANCY
1.0
.9
.8
.7
.6
.5
.4
.3
.2
.1
0
400
450
500
550
600
WAVE LENGTH IN mμ

Figure 31. Resolution of the spectrum of palladium α-furildioxime in colloidal suspension into its component bands

Solid line is the observed spectrum;

Dashed curves are the individual absorption bands;

Circles represent the sum of the individual bands.



ABSORBANCY
1.3
1.2
1.1
1.0
.9
.8
.7
.6
.5
.4
.3
.2
.1
0
300
350
400
450
500
WAVE LENGTH IN mμ

$\beta_- = 39$; and $\lambda_o = 460$ mμ, $\epsilon_o = 3250$, and $\beta = 42$. The band at 460 mμ is believed to be due to the -Pd-Pd- bonding.

It should be emphasized that the component bands are contrived to fit the experimental data and one should not put too much stock in the results. In the case of nickel α-furildioxime the shoulder on the long wavelength side of the 475 mμ band in the colloidal suspension definitely indicates the presence of a band in the region of ca. 540 mμ. For palladium α-furildioxime however, the total absorption does not indicate such an absorption band, and the resolution is more uncertain. The fact that the 460 mμ peak in palladium α-furildioxime agrees closely with the 537 mμ peak in the nickel complex, both in intensity and in band width, lends support for the results that were obtained.

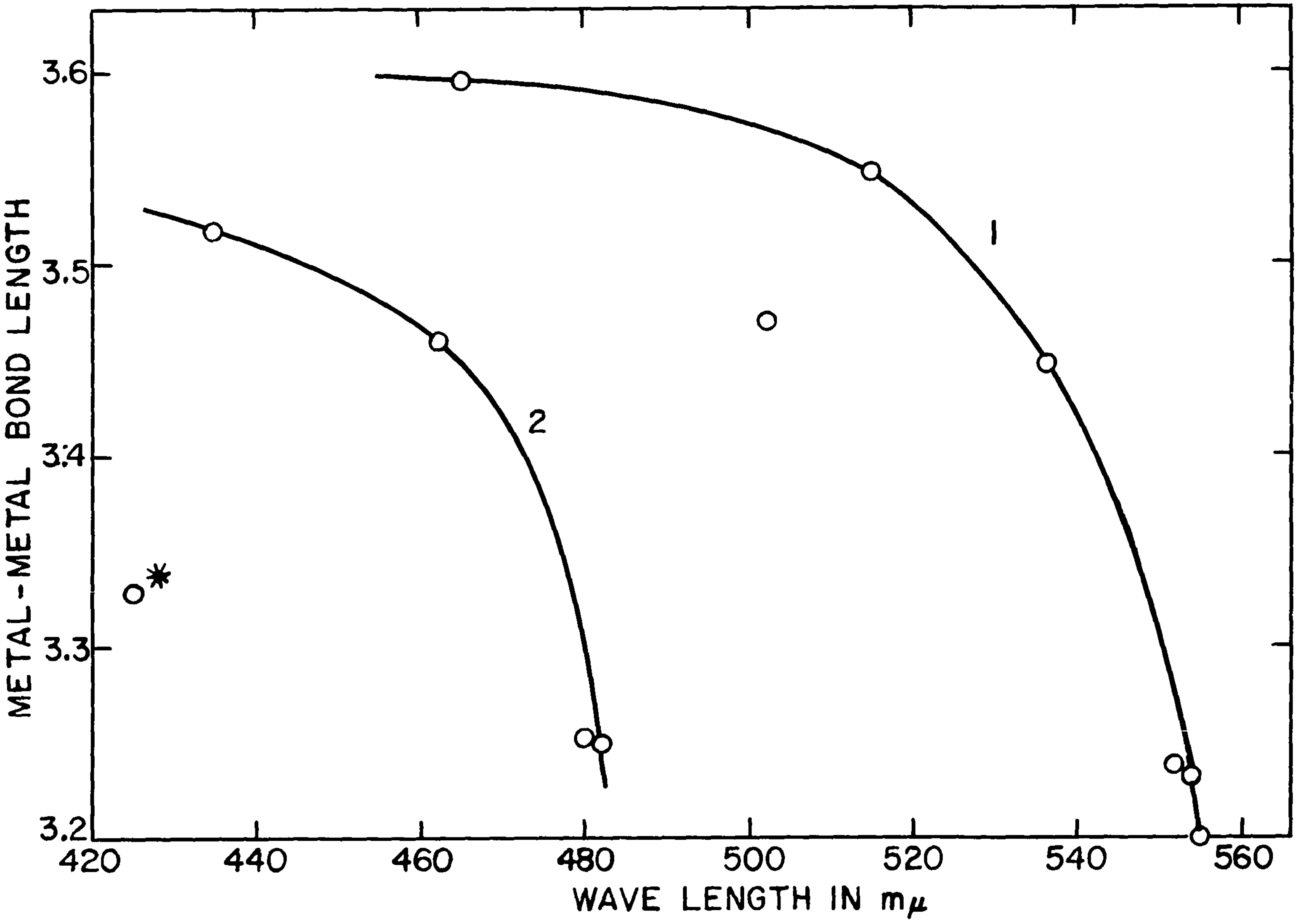
It will be noticed in Figures 30 and 31 that the agreement between observed and calculated absorption is very poor in the regions far away from the maximum. Jørgensen (48) has attributed this to the presence of undetected bands of very small intensity. This seems unlikely though, as this discrepancy seems to occur consistently in all cases. It seems more likely that the empirical equation deviates from the actual shape of the absorption bands.

In connection with the dichroism of crystals containing metal-metal bonds it was mentioned that the color seems to depend on the bond length. In Figure 32 the position of the band due to the metal chains is plotted against the metal-

Figure 32. Plot of the metal-metal bond length against the position of maximum absorption of the metal-metal absorption band in some nickel and palladium complexes

Curve 1, nickel complexes;

Curve 2, palladium complexes.


METAL-METAL BOND LENGTH
3.6
3.5
3.4
3.3
3.2
420
440
460
480
500
520
540
560
WAVE LENGTH IN mμ
1
2
*

metal bond length. It will be seen that there is a definite correlation, the band shifting to lower wavelengths as the length of the metal-metal bond increases. These data are given in Table 28.

Two separate curves were obtained; one for the nickel complexes and one for the palladium complexes. The fact that palladium α-furildioxime falls on the curve is additional evidence that the resolution of its total absorption into the component bands is correct, at least in so far that the -Pd-Pd- absorption band lies at 460 mμ.

Palladium heptoxime, which has a slightly different crystal structure than the other complexes does not fall on the curve. Thus it appears that in order for a complex to fall on this curve it must have the same crystal structure.

Also, nickel 3-methylnioxime does not fall on the curve. No explanation can be offered for this discrepancy.

The direction of this effect can be explained on the basis of the extent of delocalization of the electrons constituting the metal-metal bonds. It has long been known that in conjugated organic systems the absorption moves steadily toward longer wavelengths as the π-electrons in this system become more delocalized. It is believed that a similar situation exists in the metal-metal bonds. Delocalization is greatest in those complexes with the shortest metal-metal bonds so the absorption bands are found at longer wavelengths. As the metal-metal bond length increases the electrons become more localized on a particular metal atom and there is a corresponding shift of absorption to shorter wavelengths. Figure 32 shows that for the longer metal-metal bond lengths the position of the band is very sensitive to the bond length.

In all probability this band is the same one that gives rise to dichroism in single crystals of these complexes. However, as Hooker (45) has pointed out, the spectrum of the suspension is not the same as that of the single crystal. This can be seen by comparing Figures 15 to 19 with Figures 20 to 24. As yet, there seems to be no satisfactory explanation for this difference. Hooker showed by means of x-ray diffraction photographs that the large crystals of nickel dimethylglyoxime are the same as those obtained in the colloidal suspensions, and he attempted to explain the difference on the basis of the Christiansen effect in which particles whose dimensions are on the same order of magnitude as the wavelength of light being used selectively scatter light on the long wavelength side of an absorption band. This accounts for the fact that this band becomes broader, less intense, and shifts position when the colloidal suspension is prepared at higher temperatures, or is digested, but it does not seem possible that it could account for the large difference between the suspension and the single crystals.

It was thought that the difference might be connected with the structure of the energy band in which electrons constituting the metal-metal bonds are located. Hooker (45) measured the size of the colloidal particles and found that they are about 2000 A.U. long. Thus, each row of nickel atoms contains about 600 atoms. According to Rundle (75) this is essentially an infinite chain so that one would expect this to interact with light in the same way as the larger crystals.

One factor that may affect the absorption spectrum is that in the colloidal suspension crystals are oriented in all possible directions, while the single crystals were always oriented with the needle axis perpendicular to the light beam.

Yamasaki and Matsumoto (97) have attributed this visible absorption band in the solid complexes to the hydrogen bonding. However, hydrogen bonds exist both in the solid state and in the dissolved state, and one would not expect an appreciable change in absorption without some change in the electronic structure of the molecule. Furthermore, the Magnus green salt, $Pt(NH_3)_4^{++}, PtCl_4^{=}$, which contains -Pt-Pt- bonds, but no hydrogen bonding, shows a similar absorption band.

E. Solubility in Organic Solvents

Since Godycki and Rundle (36) proposed that the insolubility of nickel dimethylglyoxime is due to the chains of nickel atoms, one would expect that as the metal-metal bond lengths were made longer and longer they would contribute less and less to the stability of the crystal, and the solubility should increase. Thus, the solubilities of five nickel complexes and of five palladium complexes in chloroform were measured and compared with their metal-metal bond lengths. These data are shown in Table 31. It will be immediately seem that there is only a very rough correlation at best between the solubility and the metal-metal bond length. Actually, this is not surprising since the nature of the ligand varies considerably in this series.

About the only two complexes that can be compared are nickel nioxime and nickel heptoxime for which one observes an increase from 0.67×10^{-4} to 56×10^{-4} mole per liter in the solubility, accompanied by an increase in the -Ni-Ni- bond length from 3.233 to 3.596 A.U. The increase in molecular weight is small.

A similar increase is noted for palladium nioxime and palladium heptoxime although this may be a less valid comparison since the two complexes do not have the same crystal structures.

Table 31. Solubilities of some nickel and palladium complexes in chloroform and in 1,2-dichlorobenzene

Complex	-M-M- bond length	Solubility in chloroform (mole/l.)	Solubility in 1,2-dichlorobenzene (mole/l.)
nickel dimethylglyoxime	3.233	5.5×10^{-4}	2.0×10^{-4}
nickel nioxime	3.237	0.67×10^{-4}	0.32×10^{-4}
nickel α-furildioxime	3.448	16×10^{-4}	18×10^{-4}
nickel α-benzildioxime	3.547	13×10^{-4}	5.9×10^{-4}
nickel heptoxime	3.596	56×10^{-4}	13×10^{-4}
palladium nioxime	3.250	1.4×10^{-4}	-
palladium dimethylglyoxime	3.253	5.0×10^{-4}	-
palladium heptoxime[a]	3.329	89×10^{-4}	-
palladium α-furildioxime	3.459	8.1×10^{-4}	-
palladium α-benzildioxime	3.517	8.5×10^{-4}	-

[a] Palladium heptoxime does not have the same crystal structure as the other complexes in this table.

The solubilities in 1,2-dichlorobenzene were also measured. It can be seen in Table 31 that these vary in the same manner as they do in chloroform.

F. Solubilities in Water and Solubility Products

In Table 32 the solubilities in water of some nickel complexes are compared with their metal-metal bond lengths. In this table the "experimental" solubilities are those determined by measuring the amount of nickel in solution after shaking an excess of the solid complex with water for several days. Comparing these data with the -Ni-Ni-bond lengths it is evident that there is no direct correlation. This result is in contradiction to the conclusion of Sharpe and Wakefield (79) that the solubility in water increases with increasing metal-metal bond length.

The "calculated" solubilities were obtained from the solubility products, using Equation 3.12 on p. 64. The pH in these calculations was taken to be 7.0. The difference between these two columns of solubility is probably because the "experimental" solubilities are at a lower pH. Since the pH at equilibrium depends on how much of the complex has dissolved it is seen that the molar solubilities in water can be misleading when discussing the effect of metal chains. In this work the effect of metal-metal bonding will be discussed in terms of the solubility products.

Table 32. Solubilities in water of some nickel *vic*-dioxime complexes

Complex	-M-M- bond length	Solubility "experimental" (mole/l.)	Solubility "calculated" (mole/l.)
nickel dimethylglyoxime	3.233	2.1×10^{-6}	1.6×10^{-6}
nickel nioxime	3.237	1.6×10^{-6}	0.055×10^{-6}
nickel α-furildioxime	3.448	0.63×10^{-6}	-
nickel α-benzildioxime	3.547	0.70×10^{-6}	-
nickel heptoxime	3.596	0.90×10^{-6}	0.24×10^{-6}

In order to get a better picture of the factors affecting the solubility, the solubility products of nickel dimethylglyoxime, nickel nioxime, and nickel heptoxime were measured at 25° and 40°C. From these data, ΔF^{o}, ΔH^{o}, and ΔS^{o} were calculated using the equations

$$\Delta F^{o} = - R\ T \ln K_{sp}, \qquad (4.2)$$

$$\frac{d\,\Delta F}{dT} = - \frac{\Delta H}{R\ T^{2}}, \qquad (4.3)$$

and

$$\Delta S = - \frac{d\Delta F}{dT} \qquad (4.4)$$

These data are given in Table 33.

Table 33. Thermodynamic constants for the reaction $Ni(DH)_2 = Ni^{++} + 2\ DH^-$

Complex	T	K_{sp}	ΔF^o kcal.	ΔH^o kcal.	ΔS^o cal/deg/mole
nickel dimethylglyoxime	298°K	2.2×10^{-24}	32.15	12	-67
	313°K	5.9×10^{-24}	33.15		
nickel nioxime	298°K	4.1×10^{-29}	38.58	41	+ 7.3
	313°K	1.1×10^{-27}	38.47		
nickel heptoxime	298°K	2.3×10^{-27}	36.20	25	-36
	313°K	1.8×10^{-26}	36.74		

Comparing the solubility products at 25° with the molar solubilities, it is evident that the molar solubilities are misleading in their indications of the effect of the metal-metal bonds on the solubility. The solubility product for nickel nioxime is smaller than that of nickel dimethylglyoxime by a factor of 5.4×10^4, even though both complexes have about the same metal-metal bond length. On the other hand, nickel heptoxime has a solubility product which is about 56 times larger than that of nickel nioxime and this is about the effect one would expect if only the strength of the -Ni-Ni- bonds determined the relative solubility products.

The presence of nickel-nickel bonds gives rise to two effects on the solubility products of these complexes. As the strength of the metal-metal bond decreases one effect tends to increase the solubility product and the other effect tends to decrease it. This is, of course, neglecting all other factors.

In order to dissolve the solid nickel complex of a vic-dioxime it is necessary to break the -Ni-Ni- bonds. This requires energy, and will show up in the ΔH term. Writing the equation for the reaction as

$$\text{enthalpy} + \text{Ni(DH)}_2\text{(c)} = \text{Ni}^{++}\text{(aq.)} + 2\ \text{DH}^-\text{(aq.)}\ ,$$

it is clear that the stronger the metal-metal bonds the greater will be the algebraic value of ΔH.

On the other hand, the entropy of a solid compound decreases with increasing intermolecular forces (54) Since $\Delta S^o = \bar{S}^o_{Ni^{++}} + 2\,\bar{S}^o_{DH^-} - S^o_{Ni(DH)_2}$, ΔS in the above reaction will be algebraically larger for complexes with shorter metal-metal bonds.

The solubility product is related to the free energy of Gibbs through Equation 4.2. Further,

$$\Delta F^o = \Delta H^o - T\Delta S^o, \qquad (4.5)$$

so one can see that an increase in ΔH increases ΔF and therefore decreases K_{sp}, while an increase in ΔS decreases ΔF and therefore increases K_{sp}. Again it should be pointed out that all other factors except the metal-metal bonds have been neglected.

The differences between ΔH and ΔS for nickel nioxime and nickel heptoxime seem to fit this situation, at least qualitatively. Nickel nioxime has shorter, and therefore stronger, -Ni-Ni- bonds and both ΔH and ΔS are larger than for nickel heptoxime. The effect of ΔH to decrease the solubility product of nickel nioxime is apparently greater than the effect of ΔS so that a net decrease in K_{sp} is observed. Thus, it appears that in these two complexes the difference in solubility products is due to the strength of the metal-metal bonding.

However, nickel dimethylglyoxime does not fit into this picture at all. Both ΔH and ΔS are much smaller than one would expect on the basis of the metal-metal bond length alone relative to that of nickel nioxime. The factors that are responsible for this are open to speculation. The most obvious difference between nickel nioxime and nickel dimethylglyoxime is that in nioxime the oxime groups are ridgidly held by the ring so they both point in the same direction. In dimethylglyoxime, however, the oxime groups may be either cis or trans to one another due to rotation about the central C-C bond. This central C-C bond in dimethylglyoxime has about 25% double bond character (60,61) so rotation is not entirely free. Merritt and Laterman (61) have determined the crystal structure of dimethylglyoxime and shown that in the crystal the molecule exists in the trans configuration. Although this configuration is stabilized in the crystal by hydrogen bonding, it would be expected that it would also be the more stable of the two configurations in aqueous solutions. Assuming that the energy required to break the -Ni-Ni-, Ni-N, and O--H--O bonds is the same in both cases, it can be seen that $\Delta H_{Ni(DMG)_2}$ would be less than $\Delta H_{Ni(Niox)_2}$, because part of the energy will be regained by forming the more stable trans configuration of dimethylglyoxime. However, this could account for only a very small part of the observed 29 kcal. difference.

The effect of rotation about the central C-C bond in dimethylglyoxime tends to increase the value of ΔS. Rotation represents an increase in disorder, and therefore an increase in entropy of the vic-dioxime. Since $\Delta S^{o} = \bar{S}^{o}_{Ni^{++}} + 2\,\bar{S}^{o}_{DH^{-}} - S^{o}_{Ni(DH)_2}$ it can be seen that this will tend to increase ΔS. Thus, the difference in ΔS between nickel nioxime and nickel dimethylglyoxime is due to some other factor.

The entropy of a substance also depends on the molecular weight. However, this factor cancels out in these two cases.

One factor that may be responsible for at least part of the observed difference could be that nickel nioxime molecules pack in the crystal in such a manner that the van der Waals forces of attraction are stronger than in nickel dimethylglyoxime. This would tend to make both ΔH and ΔS for nickel nioxime larger than ΔH and ΔS for nickel dimethylglyoxime, as is actually observed.

At first, the negative values of ΔS were somewhat disturbing, since one would expect that the solid complex would have a lower entropy than its component ions in solution. However, this factor is apparently more than compensated for by the solvation of the nickel ions and the dioxime anions. Charles and Freiser (21) measured ΔS for the reaction

$$Ni^{++}(sol'n) + 2\,DH^{-}(sol'n) = Ni(DH)_2(sol'n)$$

in 50% dioxane-water. They found an unusually high entropy value of 106.5 e.u. which they attributed to the overall decrease in the number of particles accompanying the reaction due to solvation of the ions. Thus it can be seen that the step

$$Ni(DH)_2(c) = Ni(DH)_2(sol'n)$$

does have a positive ΔS.

V. SUMMARY AND CONCLUSIONS

In this work the following points have been demonstrated:

1) Several nickel and palladium complexes of vic-dioximes have been shown to have the same crystal structure as nickel dimethylglyoxime, or at least, a structure which contains metal-metal bonding.

2) Metal-metal bond lengths have been measured in these complexes. The length of this bond was found to vary from 3.2 to 3.6 A.U. It is believed that the metal-metal bond length depends on the Van der Waals forces of attraction as well as on the bulkiness of the vic-dioxime.

3) Metal-metal bonding gives rise to a new absorption band in the visible region of the spectrum. The position of this band depends on the central metal ion, the length of the metal-metal bonds, and the crystal structure.

4) The dichroism of single crystals of several nickel complexes was studied by measuring the absorption spectrum using plane polarized light. Those complexes with strong metal-metal bonding show "abnormal" dichroism, while complexes with very long and weak metal-metal bonds exhibit practically "normal" dichroism.

5) A correlation between the metal-metal bond lengths and the molar solubilities in water and in organic solvents was sought. This could not be established because of the wide variation in the nature of the vic-dioximes.

6) The solubility products of nickel dimethylglyoxime, nickel nioxime, and nickel heptoxime were measured at 25°C. and at 40°C. From these data ΔF, ΔH, and ΔS were calculated. The relative solubility products of nickel nioxime and nickel heptoxime can be explained on the basis of the effect of metal-metal bonding on ΔH and ΔS. The solubility product of nickel dimethylglyoxime is larger than that for nickel nioxime by a factor of over 54,000, although the metal-metal bonds in these two complexes are practically identical in length. This could not be fully explained.

VI. SUGGESTIONS FOR FUTURE WORK

1) The effect of metal-metal bonds and the nature of the vic-dioxime on the solubility products should be studied in more detail. In order to study the effect of the metal-metal bond length it would be best to have a series of complexes in which the -M-M- distance varies appreciably, while the nature of the dioxime remains essentially the same. In such a series the dioximes should be symmetrical so that there is no possibility of interference from cis and trans isomers in the metal complex.

Unfortunately, no such series of complexes exists. The nickel complexes of 3-methylnioxime and of 4-methylnioxime have quite different metal-metal bond lengths, and measurement of their solubility products should be carried out. The solubility products of two other series of dioximes that would be very interesting are the series methylglyoxime, dimethylglyoxime, methylethylglyoxime, diethylglyoxime, and methyl-n-propylglyoxime, and the series pentoxime, nioxime, heptoxime, and 1,2-cyclodecanedionedioxime.

In order to get a better idea of the effect of the dioxime itself on the solubility products, these data should also be obtained for the complexes of α-furildioxime and α-benzildioxime.

2) There is no particular reason why metal chains should be peculiar to vic-dioxime complexes. A survey of

the literature of coordination compounds of nickel(II), palladium(II), platinum(II), and gold(III) should be made to find other complexes which contain such bonding. Metal-metal bonding can be detected by comparing the absorption spectra of the complex in solution with that of the colloidal suspension, or if the orientation of the molecules in the crystal are known, from the dichroism. For example, Tschugaeff (83) prepared some nickel, palladium, and platinum complexes of benzoylpyridine-oxime which crystallize in long thin needles, are insoluble in water, and only slightly soluble in chloroform.

3) It would be very interesting to know the reason for the remarkable insolubility of nickel diaminoglyoxime. As already stated, this complex is insoluble not only in water, but in all common organic solvents except dimethylformamide and glacial acetic acid. As in the case of nickel dimethylglyoxime this would probably require that a complete determination of the crystal structure be carried out.

4) Measurement of the energy of activation for the nucleation of these crystals and of the number of molecules in a nucleus would give additional information about the effects of metal-metal bonding. Measurement of the rate of growth of the crystals would be useful information for the analytical chemist, since dimethylglyoxime cannot be used for the determination of small amounts of nickel, due to

incomplete precipitation. Even on standing overnight some nickel may remain unprecipitated.

It has been suggested by Atoji, Richardson, and Rundle (2) that the energies of activation for the nucleation of the green and pink salts of Magnus be measured. The green salt contains platinum(II) chains.

5) In this work a large difference between the absorption spectra of a single crystal and of the colloidal suspension was observed. Part of the difference can be ascribed to Christiansen scattering, as already shown by Hooker (45). A more thorough study of the effect of crystal size on the spectra of these complexes might lead to an explanation of this phenomenon.

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