1966

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Recommended Citation
Caton, John Edwin Jr., "Solubility behavior of some copper(II)- and nickel(II)-vic-dioximes " (1966). *Retrospective Theses and Dissertations*. 5350.
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CATON, Jr., John Edwin, 1940-
SOLUBILITY BEHAVIOR OF SOME COPPER(II)- AND
NICKEL(II)-VIC-DIOXIMES.

Iowa State University of Science and Technology, Ph.D., 1966
Chemistry, analytical

University Microfilms, Inc., Ann Arbor, Michigan

SOLUBILITY BEHAVIOR OF SOME COPPER(II)- AND NICKEL(II)-*VIC*-DIOXIMES

by

John Edwin Caton, Jr.

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.

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Signature was redacted for privacy.

Dean of Graduate College

Iowa State University
Of Science and Technology
Ames, Iowa

1966

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I. INTRODUCTION

Serious students of quantitative analysis are generally aware of the unique properties of the vic-dioximes for the detection and gravimetric determination of nickel. A typical statement concerning the vic-dioximes is found in the text authored by Kolthoff and Sandell (50, p. 85). ".... this reagent (dimethylglyoxime) and its analogs may be said to remain in a class by themselves. Dimethylglyoxime provides perhaps the closest approach to a specific organic reagent."

Although the unusual properties of the vic-dioximes have long been utilized in the analytical chemistry of nickel, no serious analytical chemist could avoid wondering just what the basic reasons for these unique properties might be. Thus, there have been many studies concerning the basic chemistry of the metal-vic-dioximes. The resulting knowledge of the nature of these chelates served not only to satisfy the analytical chemist's curiosity and desire to understand but also aided him in his search for more and better analytical reagents.

It has long been known that both nickel(II) and copper(II) formed complexes of the same stoichiometry with the vic-dioximes. However, the basis of some of the differing characteristics observed for these two chelates was not generally obvious. The copper complex of dimethylglyoxime is more than 5000 times as soluble as the nickel complex in aqueous solution. On the other hand in an inert organic solvent the copper chelate is slightly less soluble than nickel dimethylglyoxime.

There were essentially two areas of experimental work in this investigation. The first was a study of the hydrogen bonding in copper dimethylglyoxime, nickel dimethylglyoxime, and nickel ethylmethylglyoxime. Based on the interpretation of data from this hydrogen bonding study an explanation is offered for the similarity of the solubility of copper dimethylglyoxime and nickel dimethylglyoxime in an inert solvent.

The second study was on the solution chemistry of these three chelates in several solvents; however, this study emphasized the solution chemistry of copper dimethylglyoxime. The result of this second study was a suggested explanation for the much greater solubility of copper dimethylglyoxime compared to the solubilities of nickel dimethylglyoxime or nickel ethylmethylglyoxime in solvents not considered to be inert.

II. ABBREVIATIONS ADOPTED FOR MANUSCRIPT

There are six abbreviations that will be used throughout this manuscript. They are as follows:

1. DMG for dimethylglyoxime or 2,3-butanedionedioxime
2. EMG for ethylmethylglyoxime or 2,3-pentanedionedioxime
3. $Ni(DMG)_2$ for nickel dimethylglyoxime or bis(2,3-butanedionedioximo-N,N')nickel(II)
4. $Cu(DMG)_2$ for copper dimethylglyoxime or bis(2,3-butanedionedioximo-N,N')copper(II)
5. $Ni(EMG)_2$ for nickel ethylmethylglyoxime or bis(2,3-pentanedionedioximo-N,N')nickel(II)
6. -d indicates the oxime hydroxyl hydrogens have been exchanged for deuterium ($DMG\text{-}d_2$ would indicate deuterated dimethylglyoxime.)

Any other abbreviations found in this manuscript will be the standard abbreviations of common terms and will conform to the abbreviations set forth in the American Chemical Society publication, "Handbook for Authors of Papers in the Research Journals of the American Chemical Society".

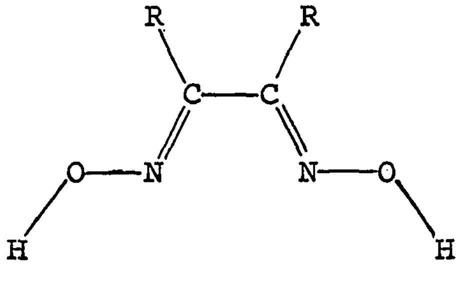
III. HISTORY OF THE METAL-VIC-DIOXIMES

In 1905 the Russian chemist, Tschugaeff (84), discovered the reaction between nickel(II) and DMG. This discovery caused much excitement in the area of analytical gravimetric precipitating reagents because of the near-specificity of DMG as a precipitant for nickel(II). Consequently, the extensive chemical literature in this field is dominated by the use of vic-dioximes as selective analytical reagents; however, much effort has also been devoted to the determination of crystal structures, magnetism, stabilities, and many other physical and chemical properties in order to understand the basis for the selectivity. Thus, the history of the metal-vic-dioximes dates back to the turn of the century and illustrates the different methods used to study coordination compounds.

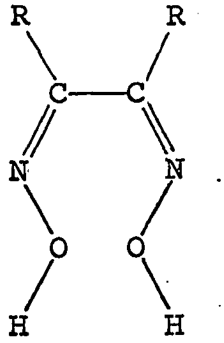
Today much of our knowledge of the chemistry of the metal-vic-dioximes is based on evidence gained from physical tools such as x-ray techniques for structure determination. However, one can hardly be less than amazed at the tremendous advances made in understanding the chemistry of the metal-vic-dioximes by earlier chemists who did not have such powerful physical tools available.

A. Early Chemistry of the Metal-*vic*-Dioximes

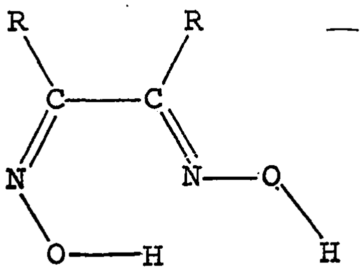
At the time of Tschugaeff's observations in 1905 the symmetric *vic*-dioximes were already known to have the following three isometric forms:



anti (α)

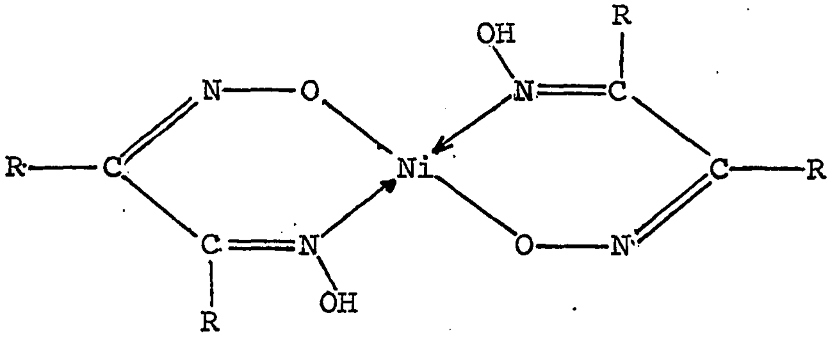


syn (β)

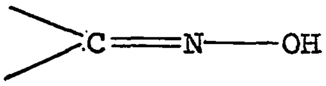


amphi (γ)

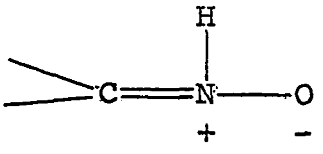
Tschugaeff (84) showed that the α-*vic*-dioximes formed isolable compounds with nickel(II), palladium(II), platinum(II), and copper(II) which had a stoichiometry of one metal ion to two ligands. In addition, he was able to demonstrate that, in the case of 2,3-hexanedionedioxime compounds with these metal ions, the cryoscopic molecular weights in benzene were close to a formula weight in which each ligand had lost one oxime hydrogen and retained the second. Due to a misconception concerning which groups interchange in the Beckman rearrangement, Werner and Pfeiffer (88) assumed that the α-*vic*-dioximes had the *amphi*-configuration. On the basis of this erroneous assumption the following structure was proposed for the nickel(II)-α-*vic*-dioxime complexes.



Soon the work of Meisenheimer (55) made it obvious that the α-dioximes had the *anti*-configuration. This evidence made the above structure proposed by Werner and Pfeiffer seem no longer feasible. Next Brady and Mehta (19) presented evidence suggesting that the oximes could exist in a zwitterion structure as well as in the classical oxime structure:

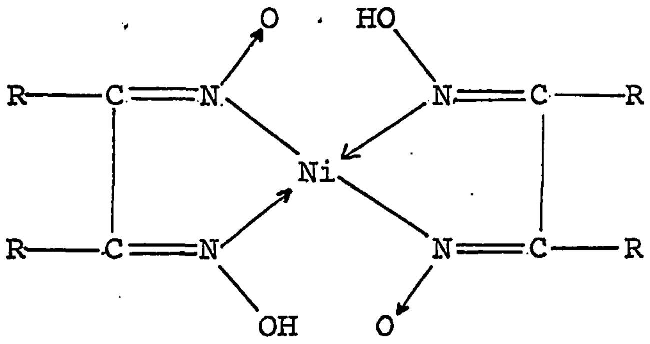


Classical



Zwitterion

On the assumption of the existence of the zwitterion form of the oxime, Pfeiffer and Richarz (65) proposed the following structure:

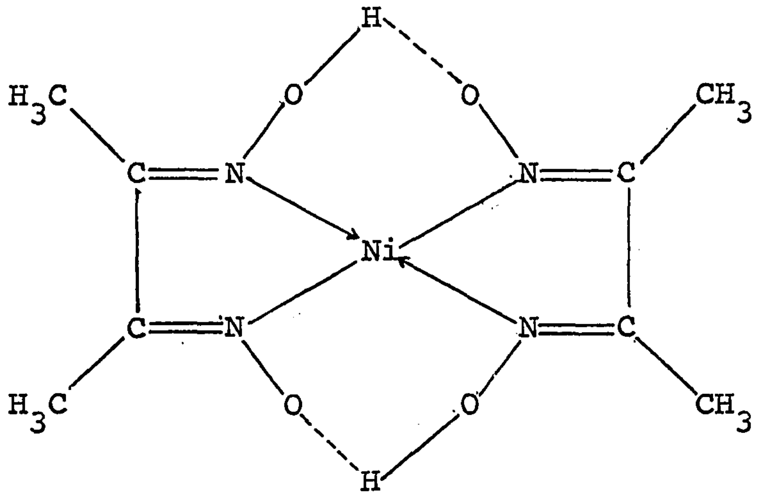


Additional evidence for this structure was provided when it was shown that the mono-O-ethers of the α-vic-dioximes react with nickel in much the same way as do the α-vic-dioximes. Pfeiffer (64) also observed that the reaction occurred even when one of the oxime groups was replaced by an imino or methyl-imino group. These observations indicated, and rightly so, that the metal-to-ligand bonding was through the oxime nitrogen atoms. However, Pfeiffer (64) also concluded that the OH group in $Ni(DMG)_2$ had no constitutional importance. Later experimental results proved this view to be not valid.

The lack of reactivity of the hydroxyl groups in the metal-α-vic-dioximes proved to be almost astounding.

Thilo and Friedrich (81) found that a suspension of Ni(DMG)$_2$ in ethanol reacted with lithium ethoxide or sodium ethoxide; however, upon addition of water this reaction was rapidly reversed. According to Tschugaeff (83) Ni(DMG)$_2$ did not react with phenyl isocyanate; and Barker (10) could not find any reaction with acetic anhydride. Barker did claim that Ni(DMG)$_2$ was methylated by methyl iodide; but Thilo and Friedrich (81) reported that they observed no reaction with either dimethyl sulfate or methyl iodide. Ni(DMG)$_2$ does not even liberate methane in the presence of methyl magnesium iodide (20), but apparently does react in a complicated manner with acetyl chloride (51). These data then indicated that the structure proposed by Pfeiffer and Richarz (65) was not entirely correct since it contained a hydroxyl group which should have reacted with all of the reagents used in the above experiments.

After Brady and Muers (20) had observed that Ni(DMG)$_2$ did not yield methane in the presence of methyl magnesium iodide in amyl ether they proposed the following structure:



This structure was based entirely on chemical evidence and the investigators did not have the benefit of the powerful physical tools available today. However, the structure resembles quite closely the structure later determined by x-ray techniques.

This brief sketch of the development of the chemistry of the metal(II)-vic-dioximes prior to the x-ray crystal structure determinations and the advent of crystal field theory demonstrates both the problems and the resourcefulness of the earlier structural chemists. However, no attempt is being made to diminish the importance of more recent techniques. For shortly after the suggested structure by Brady and Muers (20), two independent investigations indicated Ni(DMG)$_2$ to be diamagnetic. In the same year (1931) the work of Pauling (63) indicated that a diamagnetic four-coordinated nickel complex should have a square planar geometry. However, in 1932 Thilo (80) stated that Ni(DMG)$_2$ probably had a tetrahedral structure. Thus, although the earlier chemists such as Brady and Muers did brilliant work without powerful physical tools, it remained for the x-ray crystal structure determination to show with a great degree of certainty just how correct their conclusions had been.

IV. PURPOSE OF RESEARCH

The general purpose of this research was to account for the nature of the difference in the solubilities of $Cu(DMG)_2$ and $Ni(DMG)_2$.

Previous work indicated that a study of the hydrogen bonding of these chelates both in the crystalline state and in solution would reveal much about the nature of the solubilities in inert solvents. The O---O distances in some metal-vic-dioximes are the shortest ever reported for OHO bonds. Thus, a better understanding of the hydrogen bonding in metal-vic-dioximes had the possibility of contributing not only to a better understanding of the nature of the solubilities in inert solvents but also to a better understanding of very strong hydrogen bonds.

In solvents not considered inert, past studies indicated that the difference in the solubilities of $Cu(DMG)_2$ and $Ni(DMG)_2$ arose from the differing abilities of the two chelates to be solvated by various solvents. Thus, some study of the solution chemistry of these chelates seemed to be warranted by the purpose of the research.

$Ni(EMG)_2$ was utilized in this research for comparison purposes and as a substitution for $Ni(DMG)_2$ in solution studies where the latter chelate was not sufficiently soluble.

Of course, any increased understanding of compounds of analytical importance should be expected to enable the analytical chemist to improve existing methods of analyses, to develop new analytical procedures, and to formulate new analytical reagents.

V. HYDROGEN BONDING IN METAL-VIC-DIOXIMES

Undoubtedly the short OHO distances and the apparently strong hydrogen bonds of the metal-vic-dioximes are their most unique characteristics. Aside from the previously discussed investigations by early chemists concerning the extreme unreactivity of the hydroxyl hydrogen, there is much recent literature pertinent to this study.

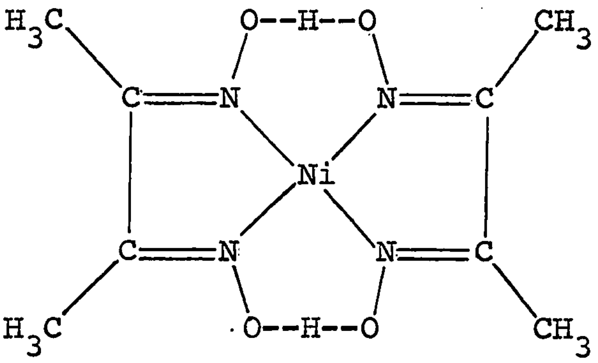
A. Literature Survey

The determination of the crystal structures of $Cu(DMG)_2$, $Ni(DMG)_2$ and $Ni(EMG)_2$ was a significant contribution to understanding the nature of the difference in the solubility of $Cu(DMG)_2$ and $Ni(DMG)_2$. Subsequent studies determined interesting thermodynamic data which led to the prediction of a hydrogen bond rearrangement in $Cu(DMG)_2$. Because this predicted hydrogen bond rearrangement was thought to play an important part in the dissolution of $Cu(DMG)_2$, an understanding of the theory of hydrogen bonds was quite pertinent to this study. Especially important to this investigation was information concerning strong hydrogen bonds occurring in OHO bridges and information concerning the effect of deuterium substitution in such bridges.

Finally this investigation employed infrared spectra to study the hydrogen bonding in these chelates; therefore, information concerning the infrared spectra of metal-*vic*-dioximes was relevant.

1. Crystal structure of the metal-*vic*-dioximes

The very short O---O distance in $Ni(DMG)_2$ provided a reasonable explanation for the significant unreactivity of the hydroxyl hydrogens. This O---O distance was originally

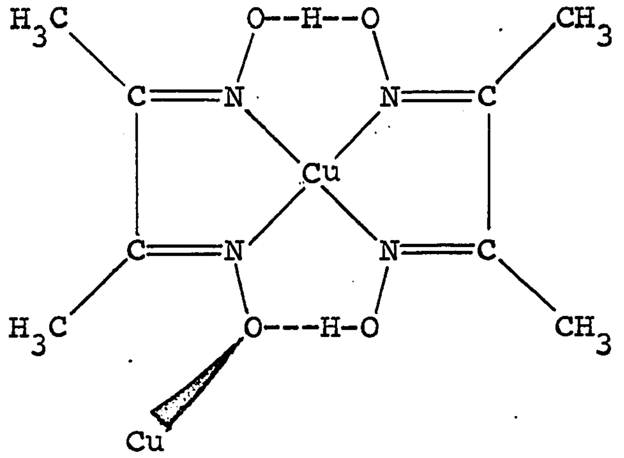


reported by Godycki and Rundle (41) to be 2.44 A, but later refinement of the data by Williams, Wohlauer, and Rundle (90) showed the O---O distance to be 2.40 A. The distance first reported was shorter than any previously reported O---O distance for an O-H-O bridge structure. Thus the inertness of the hydroxyl hydrogen was apparently due to very strong hydrogen bonding. Some investigators (41, 42, 74) suspected that symmetrical hydrogen bonds could possibly exist in $Ni(DMG)_2$.

Several other significant features appeared in the crystal structure of $Ni(DMG)_2$. The molecule was planar, and all molecules in the crystal lay in parallel planes. The molecules are stacked in the crystal so that the nickel atoms are directly over one another and spaced at a distance of 3.25 A. Alternate molecules are rotated 90° about the axis through the nickel atoms. Because the methyl groups form the bulky portion of the molecule, this 90° rotation causes the packing of the molecules in the crystal to resemble interlocking blocks.

At the time Godycki and Rundle completed their structure analysis of $Ni(DMG)_2$ the structural data for $Cu(DMG)_2$ was incomplete. However, it was known that $Cu(DMG)_2$ had a more complex packing with no chains of copper atoms. Based on the available crystal structure data and some dichroism data Godycki and Rundle speculated that the solubility differences between $Cu(DMG)_2$ and $Ni(DMG)_2$ were due to Ni-Ni bonding in $Ni(DMG)_2$. Later data proved this speculation to be partially in error.

The complete structure of Cu(DMG)$_2$ was published by Frasson, Bardi, and Bezzi (34) in 1959. While it was true that no metal-metal bonds could exist in the Cu(DMG)$_2$ crystal, the structure showed this compound to exist in the crystalline state as a dimer held together by two Cu-O bonds that were almost certainly stronger than any Ni-Ni bonds in Ni(DMG)$_2$. Another interesting fact which this crystal structure revealed was the presence of two different O---O distances in Cu(DMG)$_2$. The shorter O---O distance was 2.53 A in length and did not involve any oxygen atoms that participated in the dimer forming Cu-O bonds. The longer O---O distance (2.70 A) contained one oxygen atom that also participated in Cu-O bonding. Another feature of the Cu(DMG)$_2$ structure which was different from the Ni(DMG)$_2$ structure was that the two dimethylglyoxime ligands about



the copper atom did not lie in the same plane. The ligand that was not involved in Cu-O bonding was bent approximately 21° out of the plane of the ligand containing the oxygen atom which formed a bond with the adjacent copper atom. Thus the copper atom in $Cu(DMG)_2$ exists in a tetragonally distorted, pentacoordinated environment with four short Cu-N bonds and one longer (2.43 A) Cu-O bond.

The thorough knowledge of the crystal structures of $Cu(DMG)_2$ and $Ni(DMG)_2$ revealed several obvious differences between crystalline $Cu(DMG)_2$ and $Ni(DMG)_2$; and subsequent studies by Anderson (1) and Fleischer (33) on solubilities, stability constants, and heats of solution began to relate these differences in the crystal to differing behavior observed for the two chelates in solution. It was found that the enthalpy of solution was greater for $Cu(DMG)_2$ than for $Ni(DMG)_2$ in inert solvents such as _n_-heptane or carbon tetrachloride. In these same solvents $Ni(EMG)_2$ had a significantly lower enthalpy of solution. [$Ni(EMG)_2$ has a molecular structure (35) analogous to $Ni(DMG)_2$, but the molecules are packed into the crystal differently eliminating the possibility of Ni-Ni bonding in $Ni(EMG)_2$.]

In aqueous solution Cu(DMG)$_2$ has the lowest enthalpy of solution and Ni(DMG)$_2$ has the greatest enthalpy of solution with Ni(EMG)$_2$ being intermediate.

Rundle and Banks (73) made some very interesting predictions based on the structures and thermodynamic data. These investigators assumed that the enthalpy of solution of Ni(DMG)$_2$ in n-heptane or carbon tetrachloride should be about equal to that of Ni(EMG)$_2$ if there were no Ni-Ni bonds present in Ni(DMG)$_2$. Rundle and Banks then attributed the difference in the enthapies of solution of Ni(DMG)$_2$ and Ni(EMG)$_2$ to be a good estimate of the energy of the Ni-Ni bond in Ni(DMG)$_2$. In the case of Cu(DMG)$_2$ Rundle and Banks thought that the enthalpy of solution of Ni(EMG)$_2$ in n-heptane should be a good estimate of the enthalpy of solution of monomeric Cu(DMG)$_2$. Rundle and Banks' ideas concerning the solution of these chelates in an inert solvent are summarized in Table 1. As can readily be seen in Table 1, the case for Cu(DMG)$_2$ is more complicated than that for Ni(DMG)$_2$. If the copper chelate dissolves as a monomer, there is naturally a term for the breaking of the Cu-O bonds. However, after the Cu-O bond is broken none of oxygen atoms are involved in Cu-O bonding; thus, all oxygen

Table 1. Ideas of Rundle and Banks on dissolution of metal-*vic*-dioximes in *n*-heptane

	ΔH^o_{298} (kcal/mole)
$Ni(EMG)_2$	5.8
$Ni(DMG)_2$	14.8
$Cu(DMG)_2$	16.6

$$\underset{14.8}{\Delta H_{Ni(DMG)_2}} \approx \underset{5.8}{\Delta H_{Ni(EMG)_2}} + \underset{(9)}{\Delta H_{Ni-Ni}}$$

$$\underset{16.6}{\Delta H_{Cu(DMG)_2}} \approx \underset{5.8}{\Delta H_{Ni(EMG)_2}} + \underset{(44)}{\Delta H_{Cu-O}} + \underset{(-33)}{\Delta H_{H\text{-bond}}}$$

The numbers in this table have the units of kcal/mole. Those in parenthesis were estimated by Rundle and Banks (73). The numbers not in parenthesis were experimentally determined by Fleischer (33) or Anderson (1).

atoms can participate in hydrogen bonding to the same extent. With no logical reason for the O---O distances to remain different, a rearrangement in the hydrogen bonding is expected ($\Delta H_{H\text{-bond}}$). Rundle and Banks predicted that this hydrogen bonding rearrangement would produce much stronger hydrogen bonds such as those in $Ni(DMG)_2$ and $Ni(EMG)_2$ where the O---O distances are 2.40 A and 2.33 A, respectively.

2. Theory of OHO bonds

In 1955 Lippincott and Schroeder (52) presented a one-dimensional model of the hydrogen bond based on a potential function. The important result of Lippincott and Schroeder's model as far as the present investigation was concerned is illustrated in Fig. 1. This plot represents the difference in OH stretching frequency between a free OH bond and an OH bond occurring in an OHO bridge where R is the O---O distance. At the larger values of R this plot behaves as expected. Thus as the O---O distance becomes shorter it is expected that the hydrogen bonding will become stronger and the frequency shift logically becomes greater. However, this frequency shift reaches a maximum at an O---O distance of 2.45 A and then decreases at shorter O---O distances. Lippincott and Schroeder state that the maximum occurring in this curve corresponds to the case of symmetrical hydrogen bonding. Thus at the maximum and all shorter O---O distances the hydrogen bond and the OH bond have the same length. As the distances become shorter than 2.45 A both bonds become

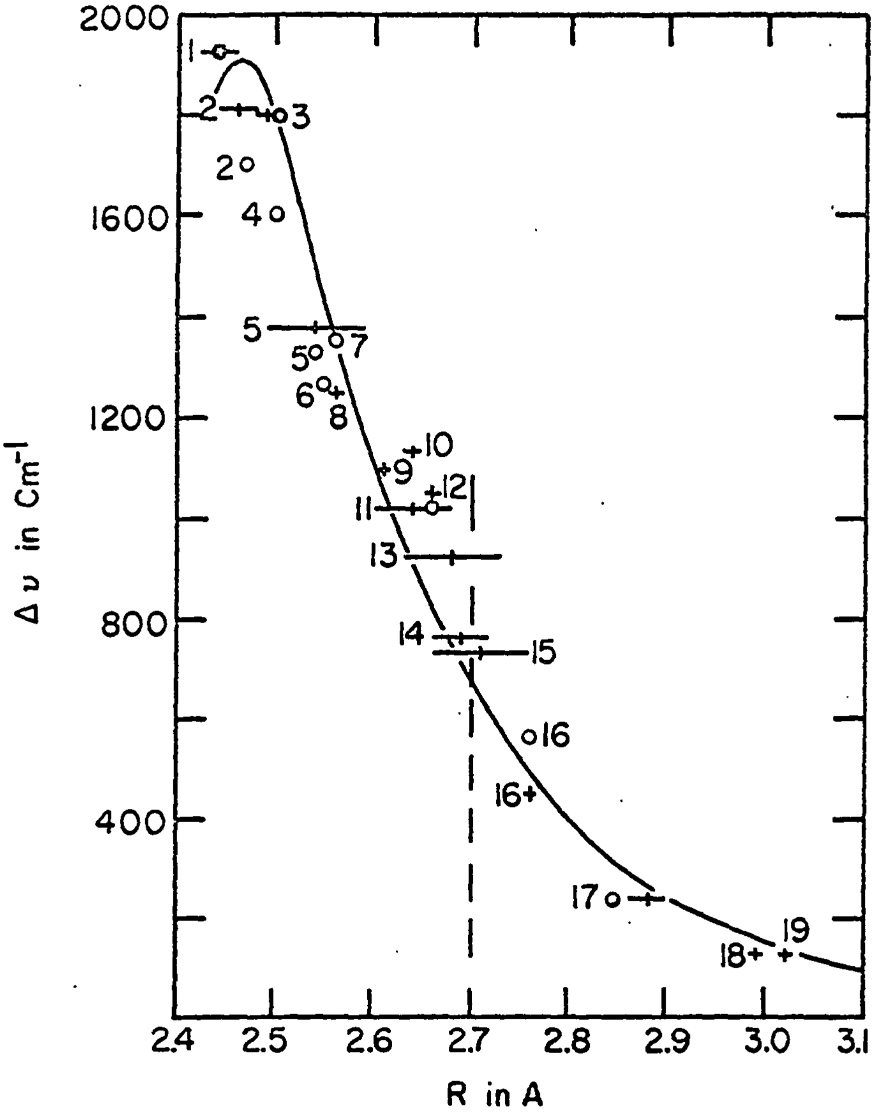


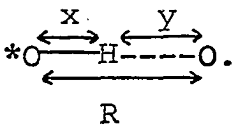
Fig. 1. Shift in OH stretching frequency as a function of O---O distance [calculated by Lippincott and Schroeder (52)]

stronger and it is to be expected that the frequency shift would decrease. Thus the model of Lippincott and Schroeder predicts that as hydrogen bonds become very strong and symmetrical the frequency of the OH stretching vibration decreases to a minimum at the point where the OHO bridge becomes symmetrical and then increases as the O---O distance becomes shorter. This behavior is summarized in Table 2.

Table 2. Summary of expectations for hydrogen bonded OH stretching vibrations based on calculations of Lippincott and Schroeder

R(A)*	y,x*	ν**	$\Delta\nu$***	OHO bond
>2.45	y > x	ν_1	$\Delta\nu_1$	asymmetrical
≈2.45	y = x	ν_2	$\Delta\nu_2$	symmetrical
<2.45	y = x	ν_3	$\Delta\nu_3$	symmetrical

$$\nu_1>\nu_2<\nu_3; \quad \Delta\nu_1<\Delta\nu_2>\Delta\nu_3$$



**ν is the OH stretching frequency.

***$\Delta\nu$ is the difference between the OH stretching frequency of a free OH [ν_0 = 3700 cm^{-1} (61)] and the hydrogen bonded OH ($\Delta\nu = \nu_0 - \nu$).

Rundle (72) made a very significant contribution to the understanding of strong hydrogen bonds in a paper published in 1964. This paper offered an explanation for the abnormal isotope effect for OHO bonds. Table 3 defines the abnormal isotope effect and summarizes the expected effect of deuterium substitution in hydrogen bonds according to the ideas of Rundle. The abnormal isotope effect is observed for O---O distances in the neighborhood of 2.50 A and is manifested by the O---O distance increasing slightly when deuterium is substituted for hydrogen in an OHO bridge. Rundle stated that the range where the abnormal isotope effect was a maximum was for O---O distances of 2.49 to 2.56 A. Rundle pictured the OHO bond as being represented by the potential wells of two normal OH bonds being forced closer and closer together as the O---O distance became shorter. This view of the OHO bond is illustrated in Fig. 2. Rundle pointed out that the zero point energy for deuterium is lower than that of hydrogen. Thus as the potential wells are pushed closer and closer together the barrier between the two wells becomes smaller. The difference in the height of the barrier which the hydrogen encounters and that which the deuterium encounters becomes quite significant as the

Table 3. Expected effect of deuterium substitution in strong hydrogen bonds

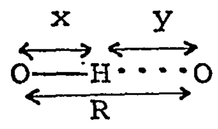
R(A)	Isotope effect[a]	O-H···O[b]
>2.55	normal	unsymmetrical
2.45 - 2.55	normal abnormal	unsymmetrical symmetrical
<2.45	normal	symmetrical

[a] Isotope effect

normal: $R_{O-H-O} - R_{O-D-O} \approx 0.005$ A
Frequency shifts as predicted by change in reduced mass.

abnormal: $R_{O-D-O} - R_{O-H-O} \cong 0.05$A
Reduced mass is not the only important factor in determining frequency shift.

[b]



unsymmetrical: $y > x$
symmetrical $y = x$

barrier becomes very small. As the O---O distance shortens to a length in the neighborhood of 2.50 A, the hydrogen has about the same probability of being located midway between the two oxygen atoms as it does of being located closer to one or the other of the oxygen atoms. However, as is illustrated for the 2.50 A O---O distance in Fig. 2, the deuterium still has a higher probability of being located nearer to one of the oxygen atoms than it does of being located midway between the oxygen atoms. Therefore, hydrogen becomes symmetrically located at a slightly longer O---O distance than deuterium. The range of the abnormal isotope effect is then the range of O---O distances where the hydrogen is effectively in a symmetrical distribution between the oxygen atoms and the deuterium still has an asymmetrical distribution. In this situation the hydrogen is associated equally with each oxygen atom and there is little distinction between the hydrogen bonding and the normal OH bond. However, in the case of deuterium, it is associated more closely with one of the oxygen atoms at a given instant causing the OD bond to be stronger than the deuterium bond. In the case of deuterium bonding in the range of the abnormal isotope effect, one of the oxygens in the ODO bridge is more loosely

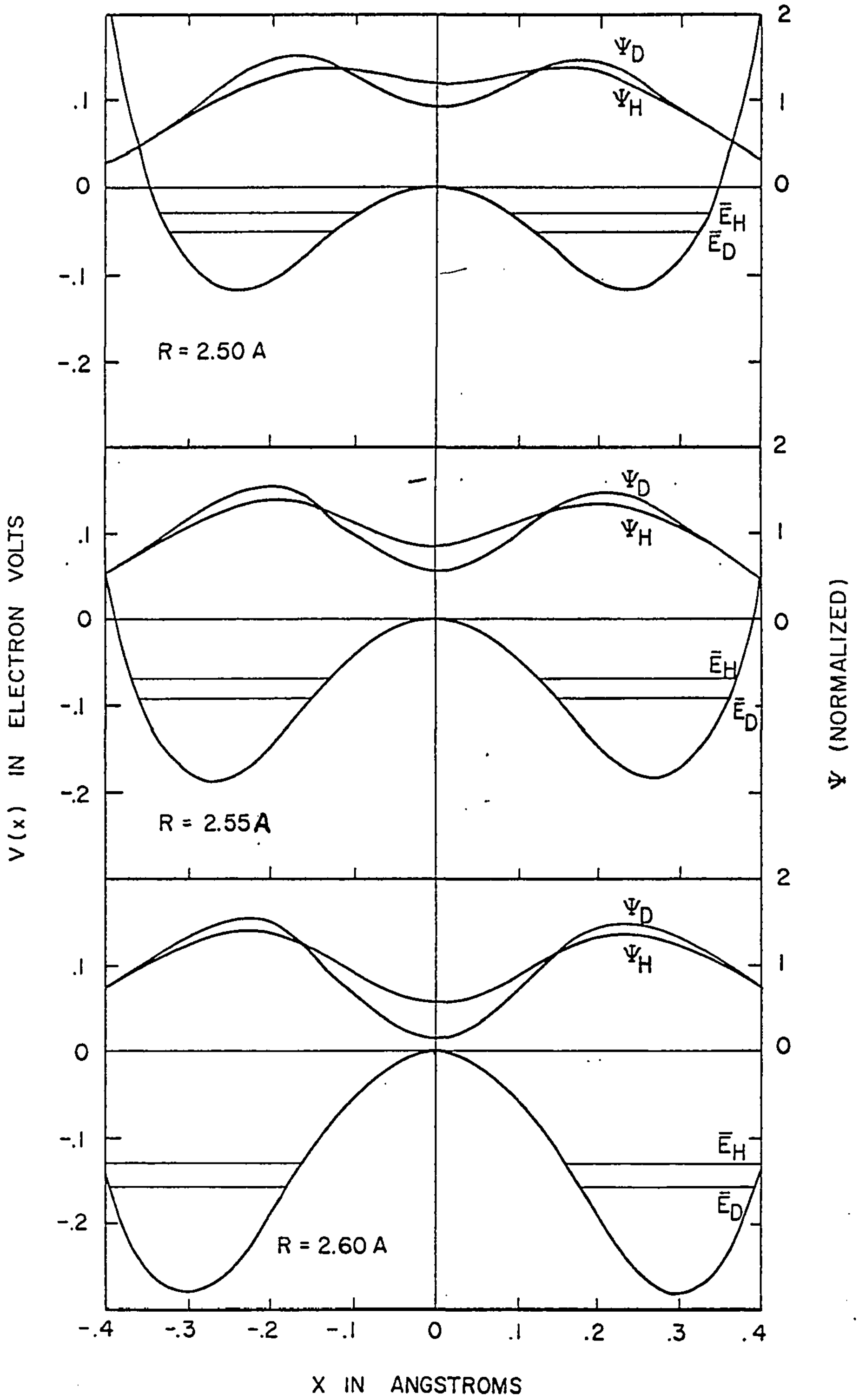


Fig. 2. Hydrogen and deuterium levels and distributions in a symmetrical double well (17)

associated and consequently the O---O distance can be longer. At O---O distances greater than the range where the abnormal isotope effect occurs, both hydrogen and deuterium are unsymmetrically distributed between the two oxygen atoms; therefore, the normal isotope effect is observed. Rundle believed that the same should be true for O---O distances shorter than the range where the abnormal isotope effect was observed. For these shorter O---O distances both the hydrogen and deuterium would be symmetrically distributed between the oxygen atoms.

Since the deuterium is more closely associated with one of the oxygen atoms in the range of O---O distances where the abnormal isotope effect occurs, the OD bond is then stronger than the OH bond for a given O---O distance. This increased bond strength causes the shift in the OH stretching frequency not to be predicted by the change in reduced mass upon deuterium substitution. Upon deuterium substitution the OH (OD) stretching frequency is normally expected to shift to a lower energy with the OD bond having a frequency that is approximately 0.7 the frequency of the OH bond. However, in the range of the abnormal isotope effect this reduced mass effect is counteracted somewhat by the stronger bond. The frequency shift approximated by the change in reduced mass upon deuterium substitution is expected only for OHO bonds with O---O distances greater or less than the range of distances where the abnormal isotope effect occurs.

A very good example of the effect which Rundle claimed is the case of $HCrO_2$ (chromous acid). Snyder and Ibers (79) have found that this molecule has an OHO distance of 2.49 A, whereas the ODO distance is 2.55 A. Thus $HCrO_2$ is an extreme case of the abnormal isotope effect. The OH stretching frequency for $HCrO_2$ is 1650 cm^{-1}. For deuterated $HCrO_2$ the OD stretching vibration is split and there are bands at 1923 cm^{-1} and 1613 cm^{-1}. Thus the change upon deuteration is very significantly different from that expected when only the change in reduced mass is considered.

3. Infrared spectra of metal-vic-dioximes

Several groups of investigators have studied the infrared spectra of the metal-vic-dioximes. These studies have mainly been concerned with the strong hydrogen bonds known to be present in these compounds. Oddly enough there is little agreement about the location of the OH stretching vibration. Some of the groups of investigators (39, 59, 60, 71, 87) have indicated that they believe the OH stretching vibration to occur in the 1700 cm^{-1} region, but others have maintained the OH stretching vibration occurs in the 2300 cm^{-1} region (13, 14, 15). The 2300 cm^{-1} band is quite weak in all spectra reported, but the assignments of Blinc and Hadzi demanded favorable consideration because they found two OH stretching bands for crystalline $Cu(DMG)_2$. These bands were at 2340 and 2650 cm^{-1}. Two bands are to be expected because the crystal structure determination revealed two different O---O distances.

Blinc and Hadzi (13) have assigned several other bands in the spectrum of $Ni(DMG)_2$. The two C═N stretching vibrations are assigned to bands occurring in the 1500 to 1600 cm^{-1}. Two NO stretching vibrations were also expected. The NO stretching vibrations were assigned to bands at 1100 and 1235 cm^{-1}. A band at 1780 cm^{-1} was assigned to the in-plane OH bending vibration, and a band at 900 cm^{-1} was attributed to the out-of-plane OH bending vibration.

Blinc and Hadzi have also claimed that $Cu(DMG)_2$ and $Ni(DMG)_2$ have a band in the 2800 cm^{-1} region. They have assigned this band along with the 2300 cm^{-1} band to the OH stretching vibration. Hadzi (43) has explained the presence of two such bands in a hydrogen bonded compound as being due to the splitting of the vibrational energy levels. According to Hadzi, this splitting takes place because of proton tunnelling. Hadzi claimed that the transition resulting from the splitting of the ground state vibrational energy level should give rise to a band in the far infrared. In the five hydrogen bonded compounds [$Cu(DMG)_2$ and $Ni(DMG)_2$ not included] which Hadzi studied, he found bands between 100 and 160 cm^{-1}. These bands disappeared upon deuteration; Hadzi believed that they shifted to frequencies below 100 cm^{-1}.

The infrared spectrum of DMG has been studied in several investigations (18, 56, 85). The assignment of the bands in this fairly simple spectrum has been fairly well established.

There appears to have been no work reported on infrared spectra of solutions of $Ni(DMG)_2$, $Ni(EMG)_2$, or $Cu(DMG)_2$.

B. Experimental Apparatus and Procedures

Much of the apparatus used in this study is common to any reasonably well equipped laboratory. Therefore, no mention will be made of such necessary equipment as glassware, mechanical stirrers and other familiar laboratory equipment.

In the case of the more sophisticated instrumentation employed, only the supplier and model will be mentioned.

Many of the chemicals utilized were from the general laboratory stock of reagent-grade quality chemicals. Thus, specific details will be given only for chemicals which were not obtained in reagent-grade quality or which were treated in some manner before use.

The procedures and preparations employed in this work will be discussed in somewhat greater detail. Because carefully obtained experimental results have some possibility of having long-range value, it seems to this author that a thorough record of how the results are obtained is important-- especially to other investigators who may wish to use the results. However, paper will not be wasted on the description of techniques commonly employed in the laboratory.

1. Instrumentation and apparatus

Infrared spectra in the 4000 to 600 cm^{-1} region were obtained on a Beckman IR-7 spectrophotometer. Far infrared spectra (800 to 33 cm^{-1}) were obtained on a Beckman IR-11 spectrophotometer. Attentuated total reflectance (ATR) spectra were obtained for the 4000 to 600 cm^{-1} region using a Barnes Engineering Company Free Reflection ATR Attachment on the Beckman IR-7. Appropriate commercially available sample cells were used for all infrared spectra.

2. Chemicals

Dimethylglyoxime was a 'Baker Analyzed' reagent. It was recrystallized twice from 1:1 ethanol-water solution.

Ethylmethylglyoxime was prepared by the oximation of the Eastman product, 2-3-pentanedione. The preparation was by N. Wilcox of this Laboratory following the procedure of Bryant and Smith (21).

Chloroform of reagent-grade quality was obtained from Allied Chemical Company. It was dried over silica gel and distilled before using.

Benzene was Mallinckrodt "purified".

n-Butylamine was a "Fisher 'Certified' Reagent".

3. Preparations and experimental procedures

$Cu(DMG)_2$ was prepared by the method of Basu, Cook, and Belfort (9). This product was analyzed for copper by the electrodeposition method described by Kolthoff and Sandell (50, pp. 407-408). The calculated percentage of copper in $Cu(DMG)_2$ is 21.63%. The electrodeposition analysis indicated 21.63 ± 0.02% copper. The copper content of the $Cu(DMG)_2$

product was also determined by EDTA titration using the method described by Fritz, Abbink, and Payne (37). Here again the results were 21.63% copper.

$Ni(DMG)_2$ was prepared by adding an aqueous solution of nickel(II) chloride to a solution of DMG in 1:1 aqueous ethanol. The mixture was made basic with aqueous ammonia.

$Ni(EMG)_2$ was prepared by slowly adding with stirring the proper amount of aqueous nickel(II) chloride solution to a heated aqueous solution containing a 2:1 mole ratio of EMG and sodium carbonate.

Both $Ni(DMG)_2$ and $Ni(EMG)_2$ were assayed for nickel using the EDTA titrimetric method of Fritz, Abbink, and Payne (37). The nickel analysis indicated that both chelates contained the correct amount of nickel to an accuracy of two or three parts per thousand.

The deuterium substituted compounds were prepared in a dry box with a dry nitrogen atmosphere. The hydroxyl hydrogens on DMG were exchanged for deuterium by dissolution of DMG in boiling deuterium oxide. The infrared spectrum indicated that the exchange was essentially complete after one such recrystallization. Nevertheless, to insure complete exchange this process was carried out three successive times.

The product of these recrystallizations was dissolved in hot deuterium oxide and combined with the proper amount of anhydrous copper(II) or nickel(II) chloride. The amount of anhydrous sodium carbonate needed to neutralize the liberated acid was then added. The mixture was digested over low heat for at least two hours. The chelates were collected by gravity filtration and kept under a dry atmosphere until they had been prepared for the determination of the infrared spectra.

$Ni(EMG)_2$ was prepared in the deuterated form in a manner analogous to that described for $Ni(DMG)_2$ and $Cu(DMG)_2$.

Infrared spectra of all solid chelates were obtained by both mull and pellet techniques. Fluorolube, halocarbon oil, and nujol mulls and potassium bromide pressed discs were employed. In most spectral regions at least two of these techniques were utilized with no significant differences in the spectra obtained. Halocarbon oil mulls appeared to yield the best spectra of these compounds in the 4000 to 1400 cm^{-1} region. In the 1400 to 600 cm^{-1} spectral region potassium bromide discs were best. At frequencies below 600 cm^{-1} a nujol mull was the only suitable technique.

Spectra of the solids were also obtained by ATR techniques. These spectra were obtained by either pressing or crystallizing the sample onto the face of a KRS-5 (thallous bromide-iodide) crystal. The crystals of $Ni(DMG)_2$ and $Ni(EMG)_2$ were small with the result that the solid material resembled powder. Therefore, it was easy to obtain good contact between the face of the KRS-5 crystal and the nickel chelates by merely pressing the sample against the face. The crystals of $Cu(DMG)_2$ prepared by the previously indicated method are large needle-shaped crystals ranging up to one-half inch in length. These crystals are hard and it was impossible to obtain adequate contact with the face of the ATR crystal simply by pressing them against the face. Sufficient contact could not be obtained even with powdered samples. Thus, $Cu(DMG)_2$ was placed on the KRS-5 crystal by evaporating solution of this chelate in ethanol on the crystal face. Such a method was slow but very good contact was achieved. In the case of $Cu(DMG)_2$-d_2 the heavy water solution was evaporated on the crystal face.

Infrared spectra of solutions of $Cu(DMG)_2$ and $Ni(EMG)_2$ along with their deuterated analogs were obtained. Matched cells were used with the reference cell containing only the solvent.

Chloroform and deuterochloroform were employed as solvents for Ni(EMG)$_2$ and Ni(EMG)$_2$-d$_2$ respectively. These solvents were fairly transparent in the 4000 to 1200 cm^{-1} range.

For Cu(DMG)$_2$ the chloroform had to be made about 0.1 M in *n*-butylamine in order that enough Cu(DMG)$_2$ could be dissolved to obtain a spectrum of significant intensity. In the case of Cu(DMG)$_2$-d$_2$ the solvent was prepared by first equilibrating 0.4 ml of *n*-butylamine with ten ml of deuterium oxide. The *n*-butylamine was then extracted into ten ml of deuterochloroform. The deuterochloroform was equilibrated with an equal volume of fresh deuterium oxide three additional times. Each equilibration consisted of shaking the two-phase mixture for one hour and then recovering the deuterochloroform phase. This solvent was dried by adding several pellets of molecular sieves. The infrared spectrum of the dried solution[1] revealed that the amine hydrogens had been exchanged. This solution was then saturated with Cu(DMG)$_2$-d$_2$,

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[1] The procedure described for the preparation of this solution was first carried out on identical volumes of *n*-butylamine, water, and chloroform. A nonaqueous titration on the final chloroform solution revealed the n-butylamine concentration to be approximately 0.1 *M*.

and the infrared spectrum of the resulting solution was obtained.

For testing the reactivity of the crystalline chelates, 10-mg samples of the solids were placed in small test tubes and covered with 20 drops of phenyl isocyanate, acetic anhydride, or dimethyl sulfate. Any immediate reaction was noted and the test tubes were stoppered and placed in a desiccator. The test tubes were observed later for any subsequent reactions.

The reactivity of saturated solutions of the chelates in benzene was checked by adding five drops of the above reagents to a ml of the benzene solution. Any color change was noted.

C. Experimental Results

The experimental data concerning hydrogen bonding was accumulated for the most part from infrared spectral studies. There were also some observations concerning the reactivity of the hydroxyl hydrogens to several appropriate organic reagents.

1. Infrared spectra

Reproductions of the infrared spectra and tables of the frequencies of the maxima are presented. The assignment of any band that was reasonably well established either in the literature or by this investigation is indicated in the tables.

The original infrared spectra usually had considerable noise in the region below 100 cm^{-1}. In reproducing the spectra this noise was smoothed out. Therefore, any bands, or apparent bands, in this spectral region are at best questionable and are not listed in the tables of band frequencies.

a. DMG The infrared spectra of solid DMG and DMG-d_2 are illustrated in Figs. 3 and 4. Some assignments and the actual frequencies of the bands are given in Table 4.

b. $Cu(DMG)_2$ The infrared spectrum of $Cu(DMG)_2$ was studied most extensively. The various spectra determined are shown in Figs. 5-8. Tables 5 and 6 list the frequencies of the bands in these various spectra.

The infrared spectrum of $Cu(DMG)_2$ was studied both in the solid and in solution. The solvent used for solution studies was chloroform that was 0.1 *M* in *n*-butylamine.

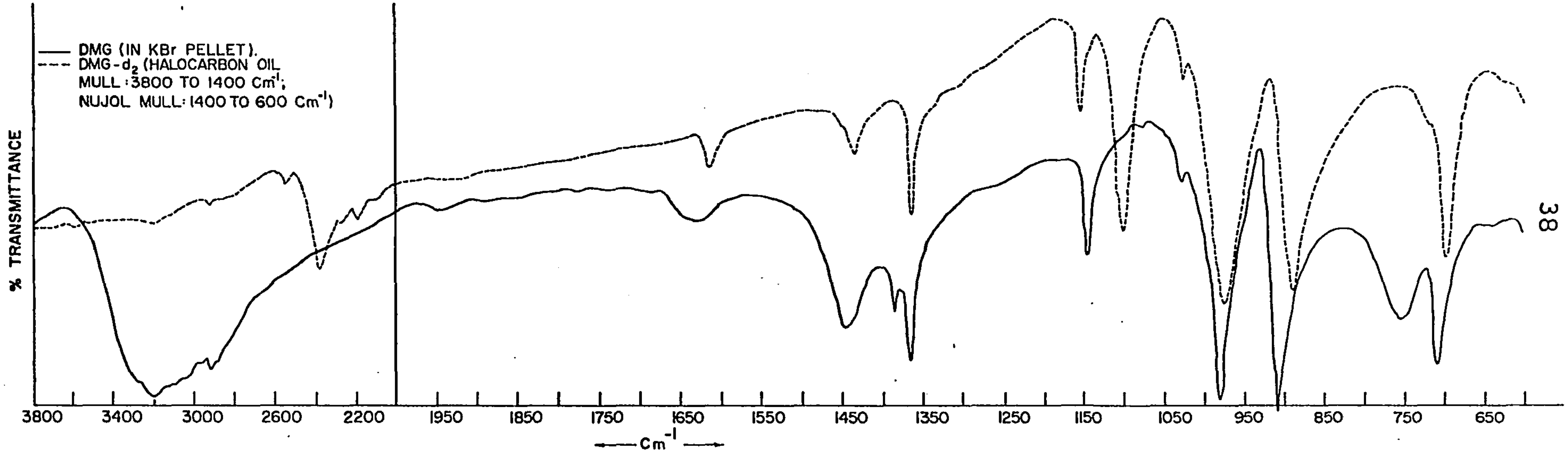


Fig. 3. Infrared spectra of crystalline DMG and DMG-d_2

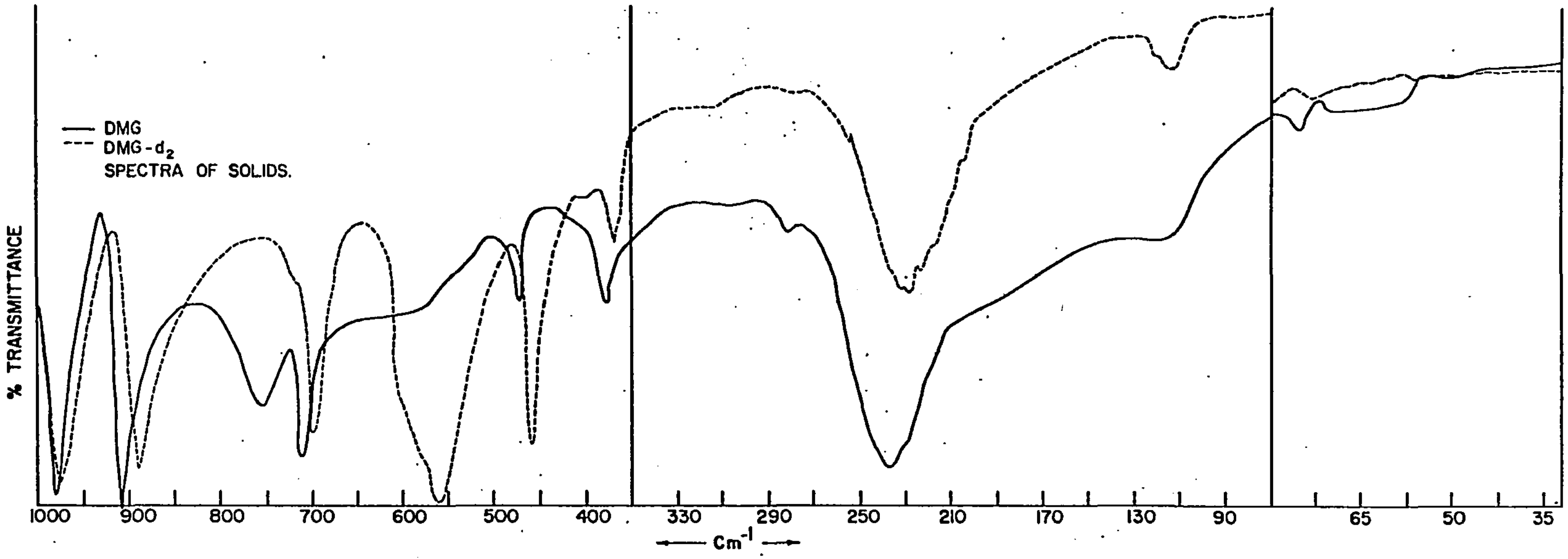


Fig. 4. Far infrared spectra of crystalline DMG and DMG-d_2

Table 4. Infrared spectra of DMG and DMG-d_2

DMG	DMG-d_2	Comments
3290*		
3200		OH stretching vibrations
3120		
3050		
2965	2968	
2930	2932	CH stretching vibrations
2885	2883	
	2522	
	2387	OD stretching vibration
	2280	
	2120	
1635	1615	CN stretching vibration (85)
1448	1436	CH bending vibrations
1366	1365	
1385		OH bending vibration
1145	1146	
	1101	OD bending vibration
1030	1030	
981	975	NO stretching vibration (85)
908	890	
756		OH bending vibration (out-of-plane)
711	699	
	563	OD bending vibration (out-of-plane)
472	461	
410		
378	370	
282		
238	228	

*All numbers in table have units of cm^{-1}.

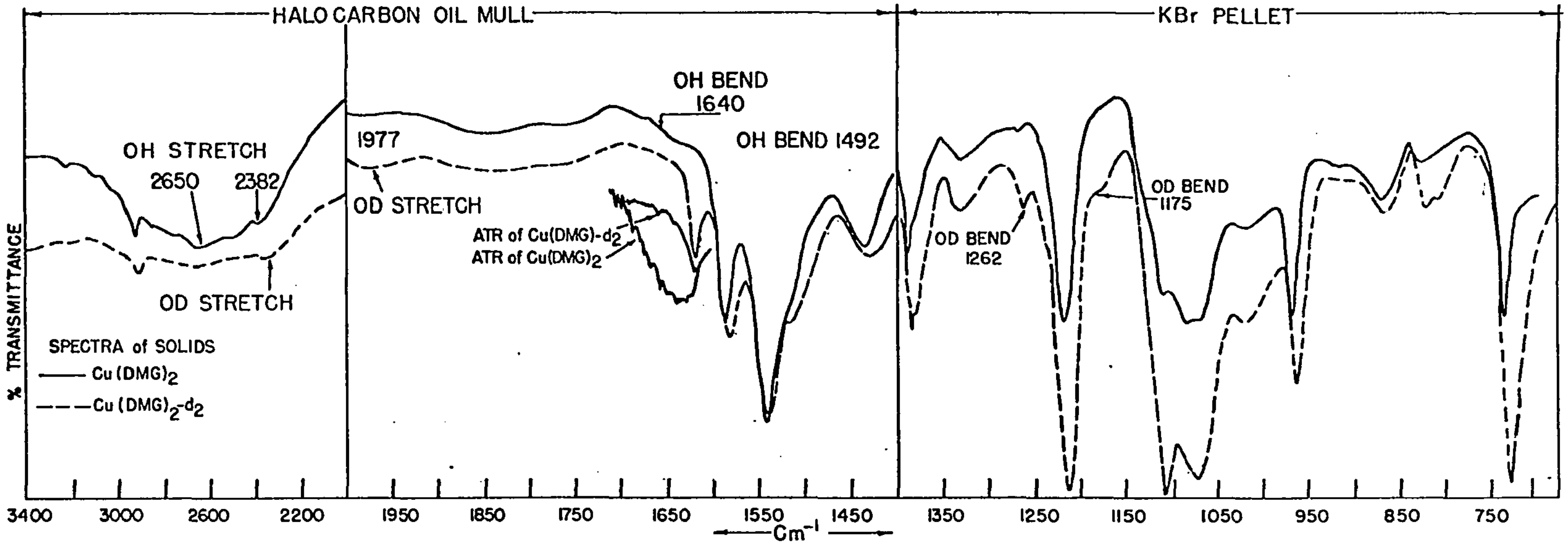


Fig. 5. Infrared spectra of crystalline Cu(DMG)$_2$ and Cu(DMG)$_2$-d$_2$

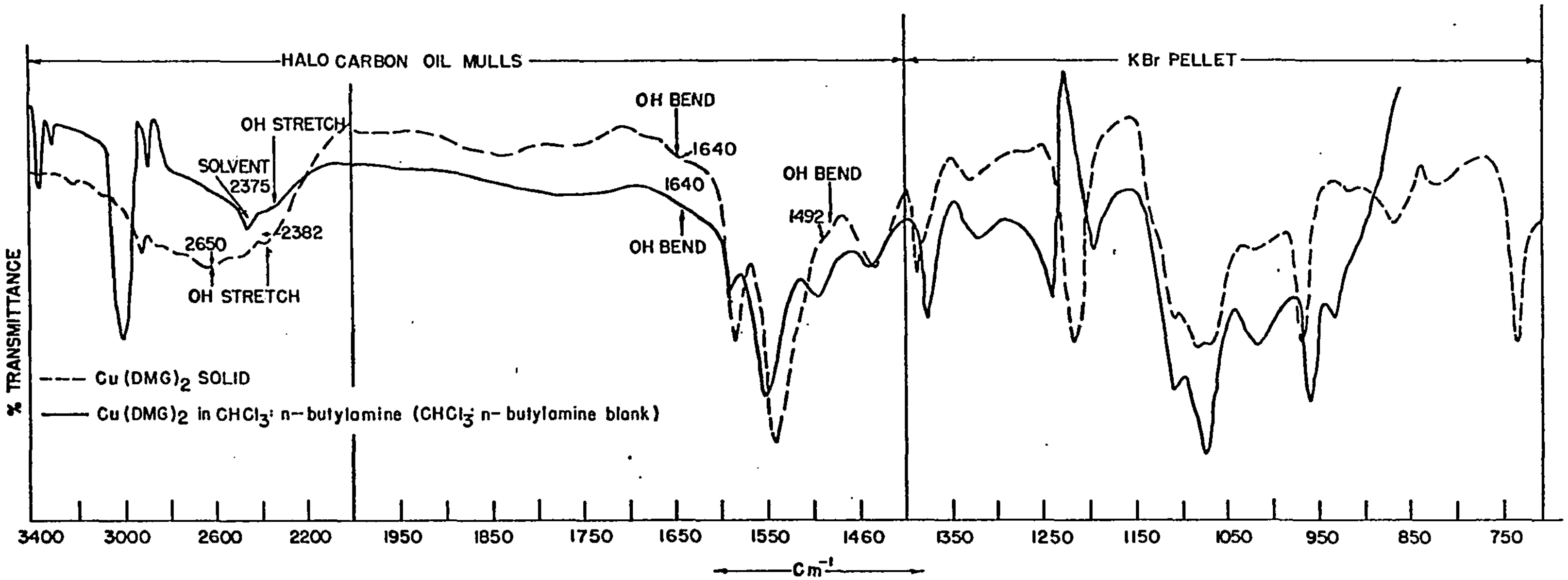


Fig. 6. Infrared spectra of $Cu(DMG)_2$ in the crystalline state and in solution

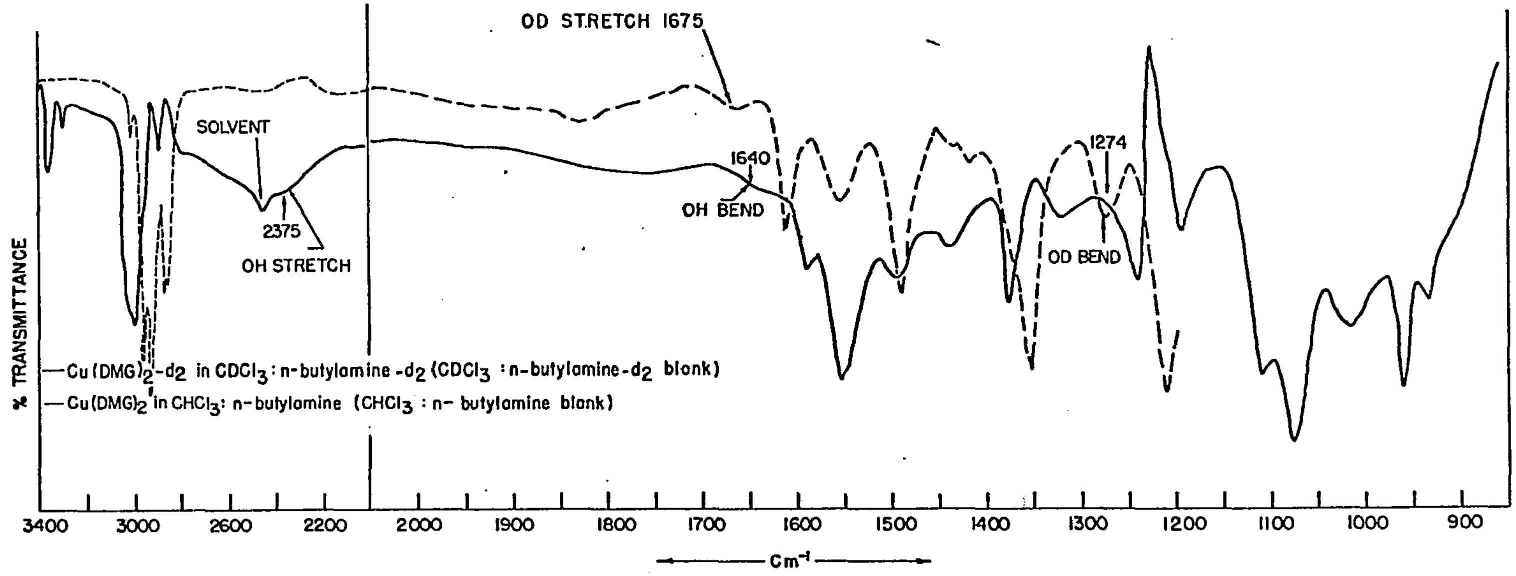


Fig. 7. Infrared spectra of $Cu(DMG)_2$ and $Cu(DMG)_2$-d_2 in solution

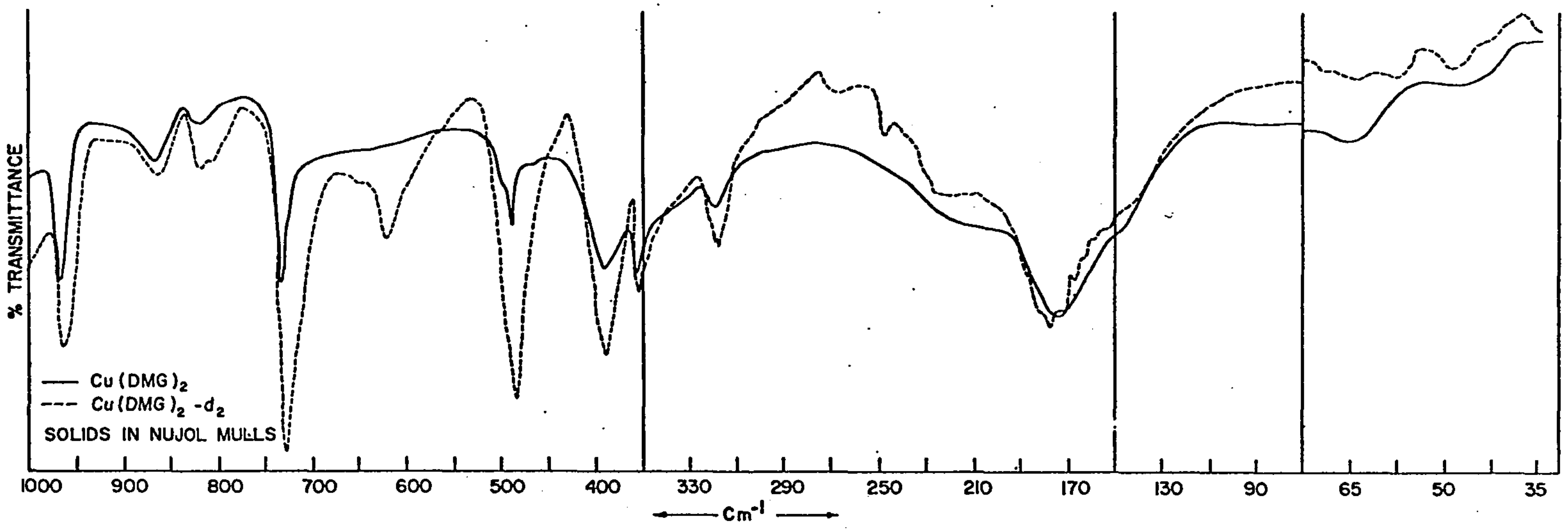


Fig. 8. Far infrared spectra of crystalline Cu(DMG)$_2$ and Cu(DMG)$_2$-d$_2$

Table 5. Infrared spectra of $Cu(DMG)_2$ and $Cu(DMG)_2$-d_2

$Cu(DMG)_2$		$Cu(DMG)_2$-d_2		Comments
solid	solution	solid	solution	
2960*	----	2970	2965	
2925	----	2930	2935	CH stretch
2852	----	2854	2876	
2650				
2382				OH stretch
	2375	2370		
		1980		OD stretch
1843	1850	1850	1835	overtone or combinations
1760	1760	1760	1736	
			1675	OD stretch
1640	1640			OH bend
1587	1594	1621	1612	CN stretch
1544	1555	1542	1555	
1518		1511		
1492				OH bend
	1497		1490	bands due to solvent
			1465	
1433	1443	1435	1421	CH bend
1379	1379	1377	1375	
1325	1325	1330	1355	
		1280	1274	OD bend
		1182		
1210	----	1212	1215	NO stretch
1072	1078	1070	1070	
1105	1110	1108	1110	CC stretch

*All numbers in the table have the units of cm^{-1}.

Table 6. Far infrared spectra of $Cu(DMG)_2$ and $Cu(DMG)_2$-d_2

$Cu(DMG)_2$	$Cu(DMG)_2$-d_2	Comments
1014*	1017	
963	963	
910	910	
864	865	
822	820	
	768**	OD bending vibration (out-of-plane)
729	724	
	625**	OD bending vibration (out-of-plane)
487	487	
390	392	
356	356	
320	320	
210	210	
174	174	

*All numbers in table have units of cm^{-1}.

**The locations of the out of plane OH bending vibrations were not established. It appeared likely that at least one of these bands was included in the broad band located at 1070 cm^{-1}. This 1070 cm^{-1} band is much broader for $Cu(DMG)_2$ than it is for $Cu(DMG)_2$-d_2.

The presence of n-butylamine enhanced the solubility of the $Cu(DMG)_2$ so that the solutions were of sufficient concentration to obtain the infrared spectrum. The actual function of the n-butylamine will be explained later in this manuscript.

The importance of ATR techniques in establishing the presence of some of the OH bands is illustrated in the 1600 cm^{-1} region of Fig. 5. The infrared spectrum of crystalline $Cu(DMG)_2$ consistently exhibited a blunt shoulder at 1640 cm^{-1} while the infrared spectrum of $Cu(DMG)_2$-d_2 did not show such a shoulder. (This observation is much more obvious on the actual spectra than it is on the reduced illustration shown in Fig. 5.) However, the ATR spectra left little doubt that a band existed in the 1650 cm^{-1} region for $Cu(DMG)_2$ but did not exist for $Cu(DMG)_2$-d_2.

c. $\underline{Ni(DMG)_2}$ The infrared spectra of $Ni(DMG)_2$ (Figs. 9 and 10) were studied only in the crystalline state. No solvent, that was suitable for use in the infrared spectral region and which would dissolve enough $Ni(DMG)_2$ to yield a significant infrared spectrum, could be found.

As was indicated in the literature survey, there has been some controversy concerning whether the 1790 cm^{-1} or

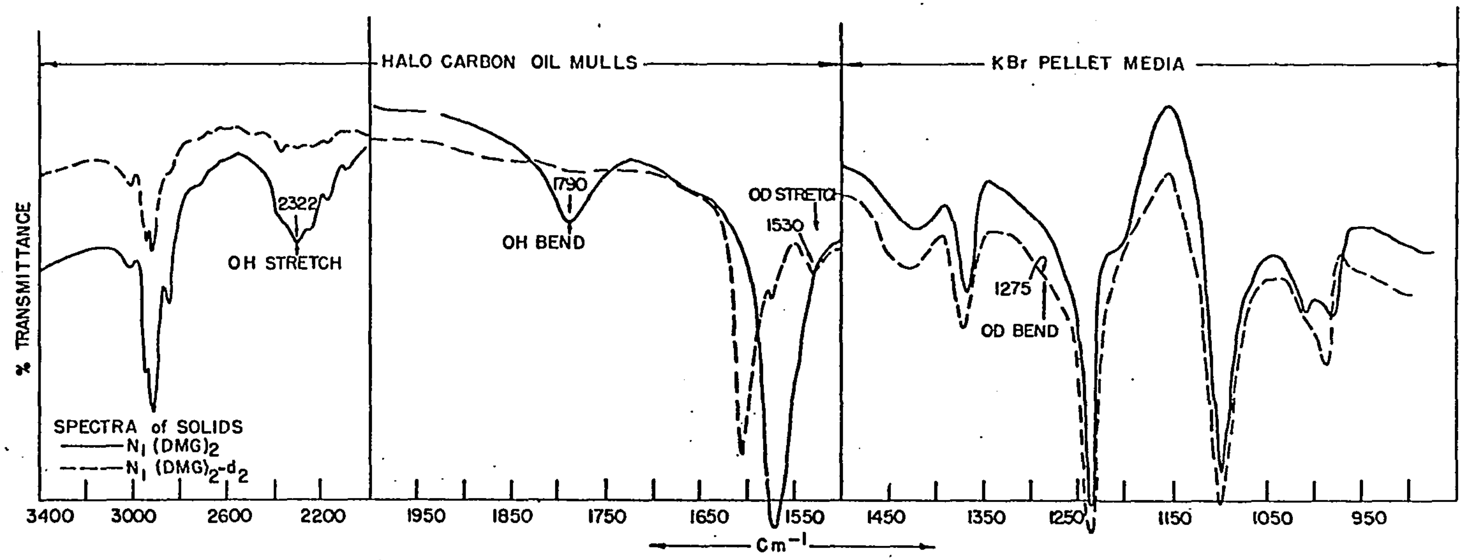


Fig. 9. Infrared spectra of crystalline Ni(DMG)$_2$ and Ni(DMG)$_2$-d$_2$

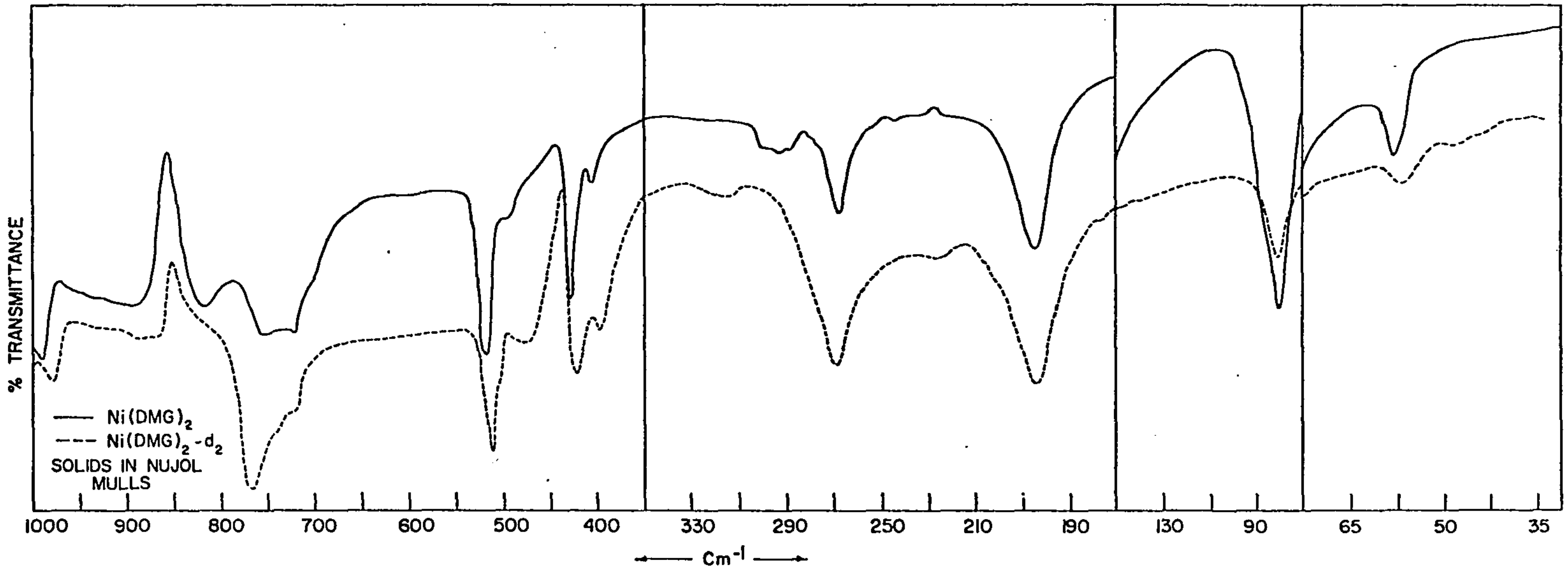


Fig. 10. Far infrared spectra of crystalline Ni(DMG)$_2$ and Ni(DMG)$_2$-d$_2$

Table 7. Infrared spectra of crystalline Ni(DMG)$_2$ and Ni(DMG)$_2$-d$_2$

Ni(DMG)$_2$	Ni(DMG)$_2$-d$_2$	Comments
2956*	2960	
2930	2932	CH stretching vibrations
2859	2862	
2469		
2379		
2322		OH stretching vibration
2267		
2137		
1790		OH bending vibration
1572	1613	CN stretching vibration
	1530	OD stretching vibration
1425	1430	CH bending vibrations
1368	1370	
	1308	OD bending vibration
	1275	
1239	1248	NO stretching vibrations
1100	1099	
1215		OH bending vibration (out-of-plane)
1005	1009	

*All numbers in table have units of cm^{-1}.

Table 8. Far infrared spectra of Ni(DMG)$_2$ and Ni(DMG)$_2$-d$_2$

Ni(DMG)$_2$	Ni(DMG)$_2$-d$_2$	Comments
991*	979	
892	880	
817	829	
754	768	
	744	OD bending vibration (out-of-plane)
710	723	
519	513	
495	476	
430	426	
406	398	
294	316	
268	268	
186	184	

*All numbers in table have units of cm^{-1}.

the 2300 cm^{-1} band was the OH stretching vibration. This controversy possibly arose because the 2300 cm^{-1} band in all previously published spectra was a very weak almost insignificant bump in the spectra.

The first spectra of $Ni(DMG)_2$ obtained in the present study also exhibited only a very weak band in the 2300 cm^{-1} region. However, it was finally discovered that if the $Ni(DMG)_2$ sample were diligently ground with a mortar and pestle in the dry state and then mulled with halocarbon oil, the well resolved band shown in Fig. 9 could be obtained. This fairly symmetrical band is centered at 2322 cm^{-1}. The band is actually more intense than the 1790 cm^{-1} band. Taking into account the effect of deuteration upon these bands there seems to be little doubt that the 2322 cm^{-1} band is the OH stretching vibration and the 1790 cm^{-1} band is the OH bending vibration.

There are several possible reasons for the improved prominence of the 2322 cm^{-1} band. The Beckman IR-7 is a better infrared spectrophotometer than the instruments used in previous investigations. Halocarbon oil was a different mulling medium from the oils used by other investigators. However, the mulling media does not appear to be a significant factor. Although the best resolution was obtained in a halocarbon oil mull, the 2322 cm^{-1} band can be reproduced in nujol mull if the sample is subjected to extended grinding before mulling. A possible reason for the weak band obtained in the past studies is that more grinding than usual is needed to resolve the band.

d. $\underline{Ni(EMG)_2}$ The infrared spectrum of $Ni(EMG)_2$ was studied in the crystalline state (Figs. 11 and 13) and in chloroform solution (Fig. 12). The spectra of crystalline $Ni(EMG)_2$ was very similar to that of crystalline $Ni(DMG)_2$. The spectrum of $Ni(EMG)_2$ in solution was quite similar to the spectrum of solid $Ni(EMG)_2$ (Table 9).

2. Reactivity of the hydroxyl hydrogen

The effect of acetic anhydride, phenyl isocyanate, and dimethyl sulfate on the three chelates in the solid state and in benzene solution was observed.

a. Acetic anhydride It was found, in agreement with Barker (10), that acetic anhydride did not affect $Ni(DMG)_2$. Acetic anhydride dissolves significant amounts of $Ni(EMG)_2$, but this reagent gave no evidence of reacting with or decomposing $Ni(EMG)_2$. However, the brown $Cu(DMG)_2$ crystals reacted upon contact with acetic anhydride to form a blue precipitate. When acetic anhydride was added to benzene

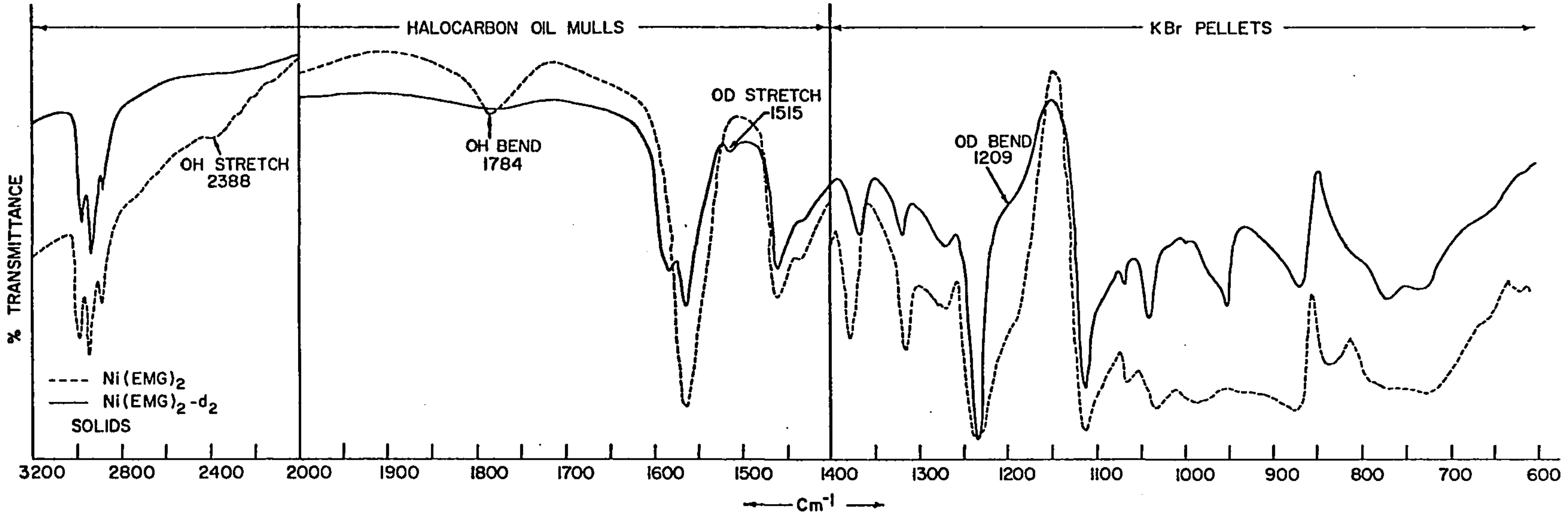


Fig. 11. Infrared spectra of crystalline Ni(EMG)$_2$ and Ni(EMG)$_2$-d$_2$

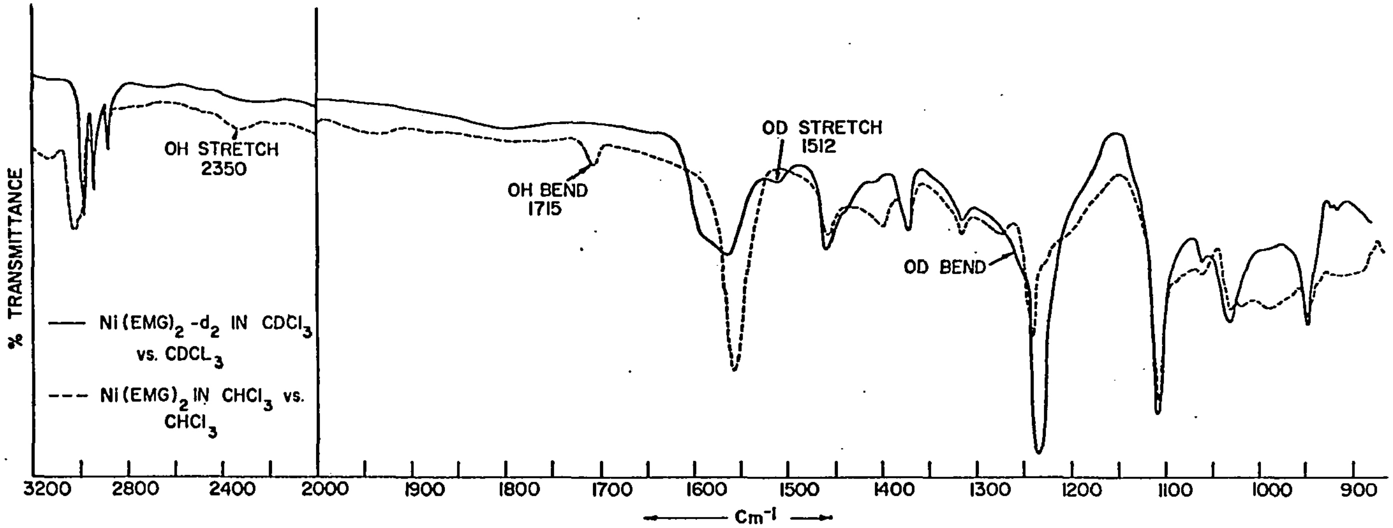


Fig. 12. Infrared spectra of Ni(EMG)$_2$ and Ni(EMG)$_2$-d$_2$ in solution

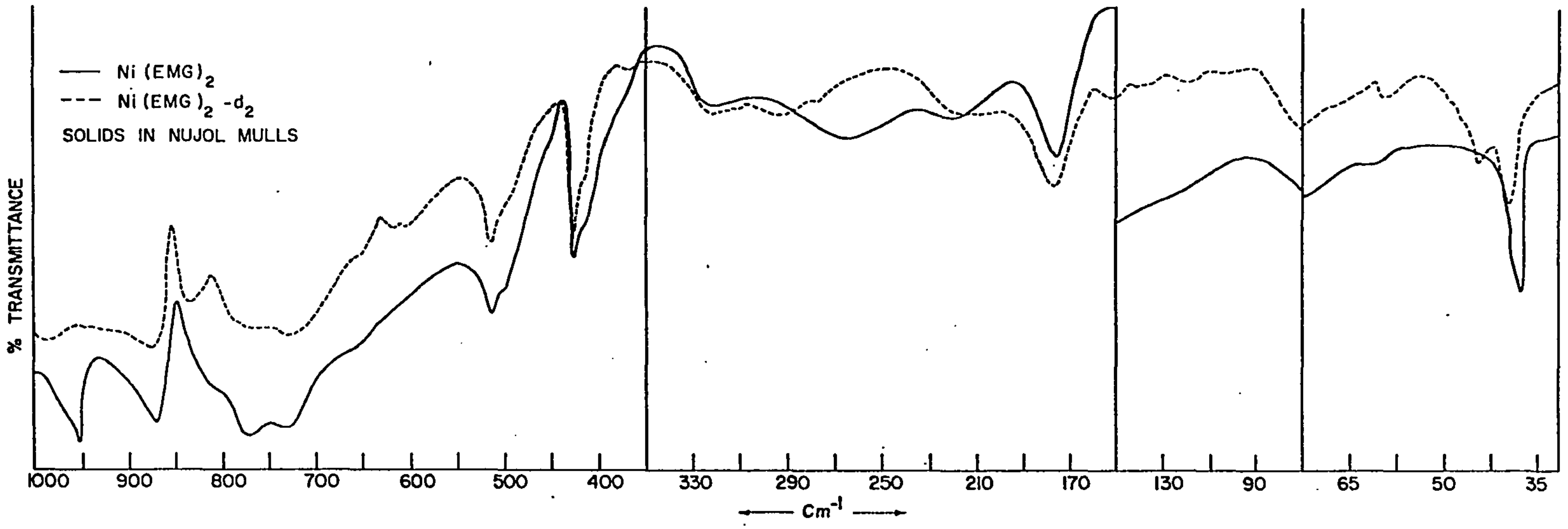


Fig. 13. Far infrared spectra of crystalline Ni(EMG)$_2$ and Ni(EMG)$_2$-d$_2$

Table 9. Infrared spectra of Ni(EMG)$_2$ and Ni(EMG)$_2$-d$_2$

Ni(EMG)$_2$		Ni(EMG)$_2$-d$_2$		Comments
solid	solution	solid	solution	
2984*	----	2985	2988	
2942	----	2944	2945	CH stretch
2881	----	2880	2833	
2388	2350			OH stretch
1784	1715			OH bend
		1583	1593	CN stretch
1563	1560	1564	1570	
		1515	1512	OD stretch
1461	1458	1459	1464	CH bend
1376	1375	1369	1375	
	1402			solvent band
1314	1321	1320	1319	
1271		1272		
1234	1235	1234	1237	NO stretch
1112	1112	1113	1111	
		1209	1253	OD bend
1064		1069		
1031		1041		

*All numbers in table have units of cm^{-1}.

Table 10. Far infrared spectra of $Ni(EMG)_2$ and $Ni(EMG)_2$-d_2

$Ni(EMG)_2$	$Ni(EMG)_2$-d_2	Comments
990*		OH bending vibration (out-of-plane)
	963	
	954	
876	872	
836		
765	774	
727	738	
	630	OD bending vibration (out-of-plane)
514	516	
429	429	
420	420	
323	324	
293	265	
211	219	
177	176	

*All numbers in table have units of cm^{-1}.

solutions of the three chelates, no color change or evidence of reaction was observed for any of the chelate solutions.

b. Phenyl isocyanate   This reagent was observed to partially decompose solid Cu(DMG)$_2$ (as evidenced by the appearance of a blue color). However, solid Ni(EMG)$_2$ and Ni(DMG)$_2$ did not appear to react with phenyl isocyanate. In benzene solution none of the three chelates appeared to react with phenyl isocyanate.

c. Dimethyl sulfate   This reagent was observed to react immediately with solid Cu(DMG)$_2$ yielding a green solution and a green precipitate. Both Ni(DMG)$_2$ and Ni(EMG)$_2$ reacted slowly with dimethyl sulfate. The former chelate slowly lost its scarlet color leaving a white precipitate, but the Ni(EMG)$_2$ dissolved completely forming a colorless solution. The reaction between dimethyl sulfate and the nickel chelates required several days, whereas similar amounts of this reagent with Cu(DMG)$_2$ brought about the described decomposition of the copper chelate in a manner of minutes. In benzene solution all three chelates appear to decompose slowly in the presence of dimethyl sulfate. Since Thilo and Frederich (81) could not find any reaction between Ni(DMG)$_2$ and dimethyl sulfate, the slow decomposition of the chelates might be due to a slow decomposition of the dimethyl sulfate to more acidic products.

D. Discussion and Conclusions

Because the main interest of this work was the nature of the hydrogen bonding in the metal-vic-dioximes, the infrared spectra were utilized to gain information concerning hydrogen bonding. The infrared data were interpreted in terms of the ideas on hydrogen bonding presented by Lippincott and Schroeder (52) and Rundle (72). The data concerning the reactivity of the chelates added evidence to the conclusions based on theory and the infrared data.

1. Nature of the OHO bond in metal-vic-dioximes

According to Rundle and Banks (73) the hydrogen bonds in crystalline Ni(DMG)$_2$ and Ni(EMG)$_2$ should be substantially stronger than the hydrogen bonds found in crystalline Cu(DMG)$_2$. On the surface it appeared that the infrared data did not indicate such a difference in hydrogen bond strengths. It is normally expected that as the hydrogen bonding becomes stronger the OH stretching frequency should decrease. However, the OH stretching vibrations for Ni(DMG)$_2$ and Ni(EMG)$_2$ were found at approximately the same frequency as one of the OH stretching vibrations in $Cu(DMG)_2$. There was a significant difference in the O---O distances (Table 11) of the three chelates which should presumably have led to a difference in the strengths of the hydrogen bonds in these compounds. The data in Table 11 can be interpreted in terms of Lippincott and Schroeder's ideas (Fig. 1). With this interpretation one can rationalize why the hydrogen bonds in $Ni(DMG)_2$ and $Ni(EMG)_2$ should be stronger than those in $Cu(DMG)_2$ and still manage to keep the explanation consistent with the infrared data. The 2.53 A O---O distance of $Cu(DMG)_2$ falls to the right of the maximum in the curve, but the shorter O---O distances of the nickel chelates fall to the left of the maximum. Thus, by this theory it is possible to have stronger hydrogen bonds and still have approximately the same OH stretching frequency.

Provided the maximum in Fig. 1 is the point where the OHO bond becomes symmetrical, it can then be concluded that the OHO bonds in both $Ni(DMG)_2$ and $Ni(EMG)_2$ are symmetrical. On the other hand, both O---O distances in $Cu(DMG)_2$ fall to the right of the maximum indicating that neither of the hydrogen bonds in $Cu(DMG)_2$ is symmetrical.

Table 11. Frequency of OH and OD bands

Chelate	State[a]	R[b]	ν_{OH}[c]	ν_{OD}[c]	δ_{OH}[d]	δ_{OD}[d]	Ref.[e]
$Cu(DMG)_2$	C	2.70	2650	1980	1518	1182	(34)
	C	2.53	2382	2370	1633	1280	(34)
	S	----	2375	1675	1635	1274	--
$Ni(EMG)_2$	C	2.34	2388	1515	1784	1209	(35)
	S	----	2350	1512	1715	1253	--
$Ni(DMG)_2$	S	2.40	2322	1537	1792	1308	(41)

[a] C is solid or crystalline state; S indicates in solution.
[b] R is OHO distance in A.
[c] ν is stretching frequency in cm^{-1}.
[d] δ is bending frequency in cm^{-1}.
[e] Reference for OHO distance.

The infrared data interpreted in terms of the ideas of Rundle (72) concerning deuterium substitution in strong hydrogen bonds complements the conclusions based on the theory of Lippincott and Schroeder. Upon deuterium substitution, the OH stretching frequency of the more strongly hydrogen bonded hydroxyl groups in $Cu(DMG)_2$ (R=2.53 A) did not shift significantly (Table 11). According to the work of Rundle, such behavior indicated that the hydrogen in the OHO bond was in an essentially symmetrical distribution but that the deuterium in ODO bond is still asymmetrically oriented between the oxygen atoms. Thus for the 2.53 A OHO bond in $Cu(DMG)_2$ the abnormal isotope effect is observed.

The difference between the OH and the OD stretching frequencies for $Ni(DMG)_2$ and $Ni(EMG)_2$ was approximately that expected due to the change in reduced mass upon deuteration. This indicated that the normal isotope effect had taken place. Because the O---O distances involved were substantially shorter than the distances at which the abnormal isotope effect was expected, it was assumed, in accordance with the theory of Rundle, that both the OHO and ODO bonds in $Ni(DMG)_2$ and $Ni(EMG)_2$ were symmetrical.

In the case of the more weakly hydrogen bonded hydroxyl group in Cu(DMG)$_2$ the O---O distance (2.70 A) was longer than the distances where the abnormal isotope effect was expected. The shift of the OH stretching frequency upon deuterium substitution was that predicted by the change in reduced mass. Therefore, both hydrogen and deuterium were concluded to have an asymmetrical orientation.

In solution the infrared spectrum of Ni(EMG)$_2$ was observed to be quite similar to the spectrum of crystalline Ni(EMG)$_2$. The bands arising from the OH and OD stretching vibrations occurred at about the same frequency both in the solid state and in solution. Thus, it is shown that the hydrogen bonding in crystalline Ni(EMG)$_2$ is not affected in a significant manner upon solution in chloroform.

The case was different for Cu(DMG)$_2$ in solution. The more energetic OH stretching vibration (2650 cm^{-1}) disappeared upon solution indicating that the weaker hydrogen bond was no longer present. Instead a single OH stretching band appeared at the approximate location of the band arising from the more strongly hydrogen bonded hydroxyl group in solid Cu(DMG)$_2$. The spectrum of Cu(DMG)$_2$-d$_2$ in solution was also different from the spectrum of Cu(DMG)$_2$ in solution (Fig. 7). The OH band occurring at 2382 cm^{-1} for dissolved $Cu(DMG)_2$ shifted to 1675 cm^{-1} upon deuterium substitution. This shift indicated that the OHO bonds giving rise to this band were no longer in the range of the abnormal isotope effect. This behavior of the spectra of $Cu(DMG)_2$ and $Cu(DMG)_2$-d_2 in solution was practically identical to that observed for $Ni(EMG)_2$ in solution and for $Ni(DMG)_2$ and $Ni(EMG)_2$ in the solid state. Apparently the hydrogen bonding of $Cu(DMG)_2$ in solution was similar to the hydrogen bonding present in the solid nickel chelates.

The observations of the effect of phenyl isocyanate, dimethyl sulfate, and acetic anhydride on the chelates both in the crystalline state and in solution yielded additional evidence for the conclusions indicated by the interpretation of the infrared data. The above reagents reacted with crystalline $Cu(DMG)_2$ quickly while reacting slowly or showing little tendency to react with the two nickel chelates. This was taken to indicate that the hydrogen bonding was substantially weaker in crystalline $Cu(DMG)_2$ than in crystalline $Ni(DMG)_2$. In benzene solution all three chelates seemed to show the same high degree of inertness toward these reagents.

Thus, the hydrogen bonding for all three chelates in solution is similar and evidentally quite strong.

Contrary to the work of Blinc and Hadzi (13), this study of the infrared spectra did not find any band near 2800 cm^{-1} which might be attributed to the OH stretching vibration. According to the work of Hadzi (43), a band should have shifted in the far infrared spectral region upon deuteration if the OH stretching vibration had been split. However, upon deuteration the far infrared spectra for each of the chelates was practically identical to the spectra for the chelates in the hydrogen form. Thus, according to the criterion set up by Hadzi, there is apparently no proton tunnelling taking place in these chelates. Of course, proton tunnelling could not be expected in any truly symmetrical hydrogen bonds. Therefore, the conclusion that the hydrogen bonds in $Ni(DMG)_2$ and $Ni(EMG)_2$ and the stronger hydrogen bond in $Cu(DMG)_2$ were symmetrical OHO bonds is consistent with the work of Hadzi (43). Apparently, the weaker hydrogen bond in solid $Cu(DMG)_2$ was too weak for one to observe the effects in the far infrared spectrum described by Hadzi.

2. Summary

The data on reactivity coupled with the infrared evidence have added very substantial support to the prediction of Rundle and Banks that the OHO bonds in $Cu(DMG)_2$ rearranged upon solution to become significantly stronger. The infrared data interpreted in terms of Rundle's explanation of the abnormal isotope effect (72) have indicated that solid $Ni(DMG)_2$ and $Ni(EMG)_2$ have symmetrical OHO and ODO bonds. On the other hand, the infrared data have shown crystalline $Cu(DMG)_2$ to have two different OHO bonds. The more weakly hydrogen bonded OHO bond in solid $Cu(DMG)_2$ was found to have asymmetrical arrangements for both the OHO and the ODO bonds. The more strongly hydrogen bonded OHO bond in $Cu(DMG)_2$ had the hydrogen in a symmetrical arrangement and deuterium in an asymmetrical arrangement. Upon solution both OHO bonds in $Cu(DMG)_2$ became identical, and both deuterium and hydrogen were found to exist in symmetrical arrangements. Finally, it is predicted that the O---O distance of $Cu(DMG)_2$ in solution should be significantly shorter than either of the O---O distances in the crystal. This O---O distance should be approximately the same as the O---O distances found in crystalline $Ni(DMG)_2$ and $Ni(EMG)_2$.

Based on work of Rundle and Banks (73) and the knowledge gained from this hydrogen bonding study, the following comments can be made concerning the nature of the difference in the solubilities of Ni(DMG)$_2$ and Cu(DMG)$_2$ in inert solvents. The rearrangement in the hydrogen bonds of Cu(DMG)$_2$ upon solution provides the necessary energy of solution to make Cu(DMG)$_2$ about as soluble as Ni(DMG)$_2$ in an inert solvent. This rearrangement makes the hydrogen bonding in Cu(DMG)$_2$ quite similar to the hydrogen bonding of crystalline Ni(DMG)$_2$ and Ni(EMG)$_2$ and to the hydrogen bonding of Ni(EMG)$_2$ in solution. Thus, in an inert solvent Ni(DMG)$_2$ and Cu(DMG)$_2$ are identical except for a different central metal ion. The hydrogen bonding is the same in solution and intermolecular forces, such as Ni-Ni and Cu-O bonds, have been removed. Therefore, the much greater solubility of Cu(DMG)$_2$ in solvents such as water must arise from some property unique to either the copper or the nickel.

E. Corollary to Hydrogen Bonding Study

There have been several studies (53, 61, 66, 74) in which plots of the OH stretching frequency shift versus O---O distance were presented. Two of these studies (53, 66) attempted to draw straight lines through the data. However, the plots published by Nakamota, Margoshes, and Rundle (61) and Rundle and Parasol (74) did have some curvature. Only the study of Rundle and Parasol showed any indication of the maximum that the calculations of Lippincott and Schroeder (52) revealed for this curve. There is a very simple explanation for the failure to locate this maximum. All these studies accepted the 1790 cm^{-1} band as the OH stretching vibration for $Ni(DMG)_2$. Thus the resulting frequency shift for $Ni(DMG)_2$ was over 500 cm^{-1} greater than if the correct OH stretching frequency had been assumed. The O---O distance of $Ni(DMG)_2$ was the only O---O distance used in these studies which was substantially shorter than the O---O distance where Lippincott and Schroeder calculated the maximum to occur. When this erronous point was plotted, there was very little indication of a substantial irregularity or maximum in the plot. (See Fig. 14.) The correct frequency shifts for $Cu(DMG)_2$, $Ni(DMG)_2$, and $Ni(EMG)_2$ are plotted along with additional points from a previous study in Fig. 14. A glance at Fig. 14 should convince the reader that the curve calculated by Lippincott and Schroeder describes the frequency shifts observed better than the plots incorporating the incorrect OH stretching frequency for Ni(DMG)$_2$. The data for the points shown in Fig. 14 are given in Table 12.

Table 12. OH stretching frequencies of some hydrogen bonded compounds

Compound	O---O distance(A)	ν*	$\Delta\nu$*
$Ni(EMG)_2$	2.33	2388	1312
$Ni(DMG)_2$	2.40	2311	1378
Maleic acid**	2.46	1890	1810
Oxalic acid dihydrate**	2.49	1900	1800
Urea oxalate**	2.50	2100	1600
$Cu(DMG)_2$	2.53	2382	1318
KH_2PO_4**	2.54	2320	1380
$NaHCO_3$**	2.55	2440	1260
Phloroglucinol**	2.56	2450	1250
$KHCO_3$**	2.61	2600	1100
Succinic acid**	2.64	2680	1020
Pentaerythritol**	2.69	2939	761
$Cu(DMG)_2$	2.70	2650	1050
Quinhydrone**	2.71	3055	645
Ice**	2.76	3156	544
Oxalic acid dihydrate**	2.88	3460	240
NaOH**	3.02	3571	121

*ν is the OH stretching frequency for the given compound. The frequency for the stretching vibration of a free OH bond was assumed to be 3700 cm^{-1} (61). Thus, $\Delta\nu = 3700 - \nu$.

**All data for these compounds was taken from Reference 61.

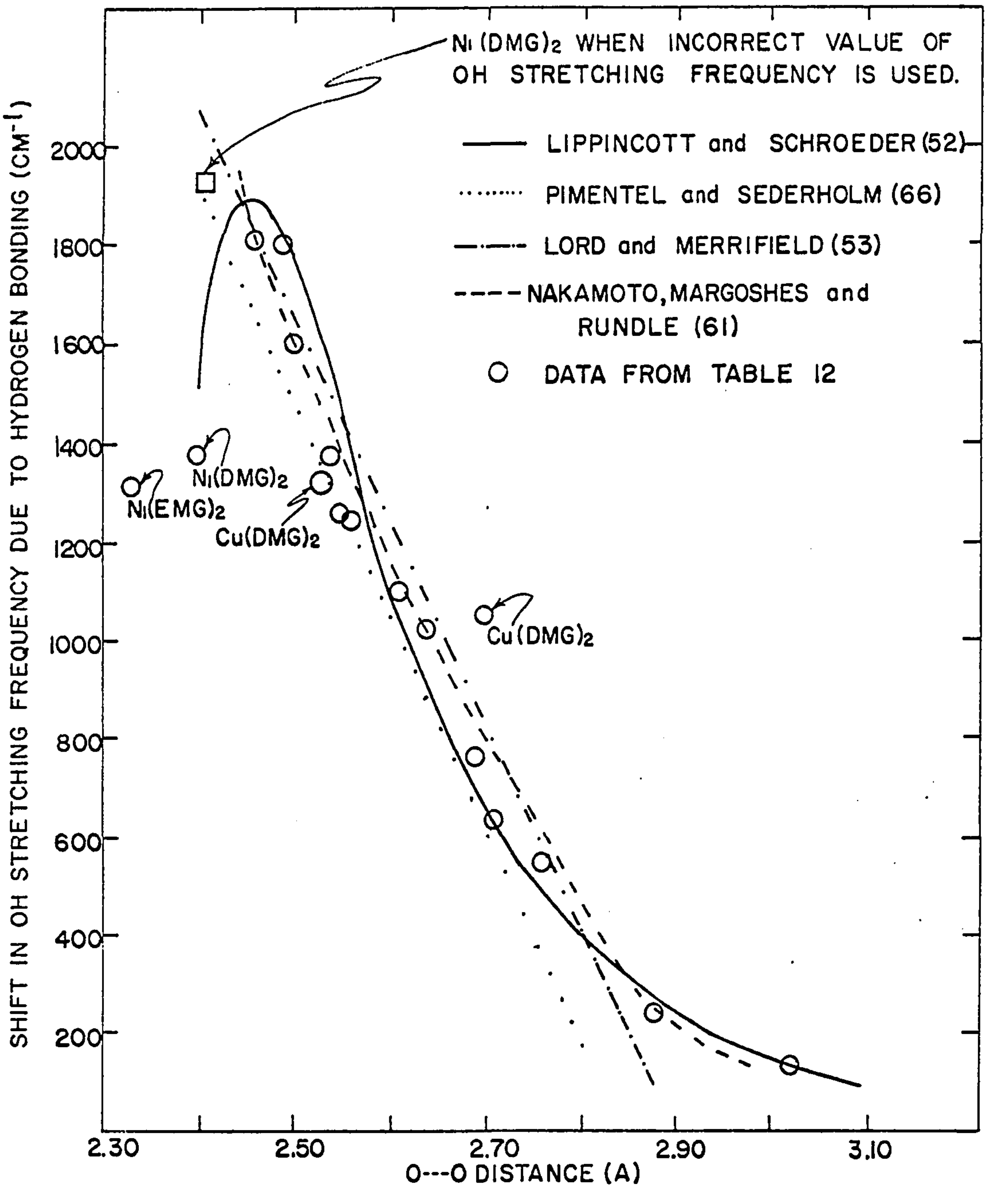


Fig. 14. Comparison of different hydrogen bonding studies

VI. SOLUTION CHEMISTRY OF THE METAL-VIC-DIOXIMES

In solvents such as chloroform and water $Cu(DMG)_2$ is known to be more soluble than $Ni(DMG)_2$. The rearrangement of the hydrogen bonds in $Cu(DMG)_2$ as it dissolves explains rather well why $Cu(DMG)_2$ is about as soluble as $Ni(DMG)_2$ in an inert solvent, but some other phenomena must account for the increased solubility of $Cu(DMG)_2$ compared to $Ni(DMG)_2$ in the more active solvents.

A. Literature Survey

There is some published work on studies of the ultraviolet and visible spectra of the metal-vic-dioximes in solution. However, much of the work deals with the utilization of these spectra for analytical purposes. There is not a great volume of literature devoted to interpreting the ultraviolet and visible spectra of the metal-vic-dioximes in solution. Thus some mention of spectral studies on copper acetylacetone, a chelate similar to $Cu(DMG)_2$ in several ways, will be included in the literature survey.

Many solvent extraction studies of the metal-vic-dioximes are found in the literature. Naturally, not a few of these studies were utilized mainly for metal analysis.

However, a few, especially those by Dyrssen (28-30), have been devoted to elucidating the solution chemistry of the metal-vic-dioximes.

Some recent work concerned with the electron paramagnetic resonance (EPR) spectra of Cu(DMG)$_2$ has made valuable contributions to the understanding of the solution chemistry of Cu(DMG)$_2$.

1. Ultraviolet and visible spectra

The effect of organic bases on the spectra of Cu(DMG)$_2$ in solution has been noted by Dyrssen and Petkovic (30). These investigators have pointed out that the intensity of some of the bands increased with the addition of organic bases. By assuming that the increased intensity was due to the greater molar absorbtivity of the Cu(DMG)$_2$ adduct with *n*-butylamine compared to the molar absorptivity of free Cu(DMG)$_2$, Dyrssen and Petkovic calculated a constant for the interaction of Cu(DMG)$_2$ with organic bases.

In conjunction with the work of Dyrssen and Petkovic, Roos (69) attempted to resolve the spectra of Cu(DMG)$_2$ with these various bases by a least squares method which he developed. However, the visible portion of the spectra was not resolved into its components by Roos.

Belfort, Calvin, and Belfort (12) have studied the spectra of copper acetylacetone in various solvents. These investigators have found that the spectra of this square planar complex differs with the solvent. By isolating the components of the visible spectra in various solvents, they have shown that the energy levels giving rise to the visible spectrum of copper acetylacetone lay at different points along the energy level diagram (Fig. 15). This is the energy level diagram for the d-orbitals on a copper(II) ion in a tetragonally distorted field. The extremities of the diagram would represent a copper(II) complex with perfect octahedral structure and a copper(II) complex with a perfect square planar structure. Belfort, Calvin, and Belfort found that in a solvent that was quite inert, the three d-electron transitions for copper acetylacetone indicated a nearly square planar complex. However, when a better donor solvent such as pyridine was used, both the $d_{(z^2)} \rightarrow d_{(x^2-y^2)}$ and the $d_{(xz)}$, $d_{(yz)} \rightarrow d_{(x^2-y^2)}$ transitions shifted toward lower energy. As expected the $d_{(xy)} \rightarrow d_{(x^2-y^2)}$ transition was less sensitive to solvent changes and remained at about the same energy regardless of solvent.

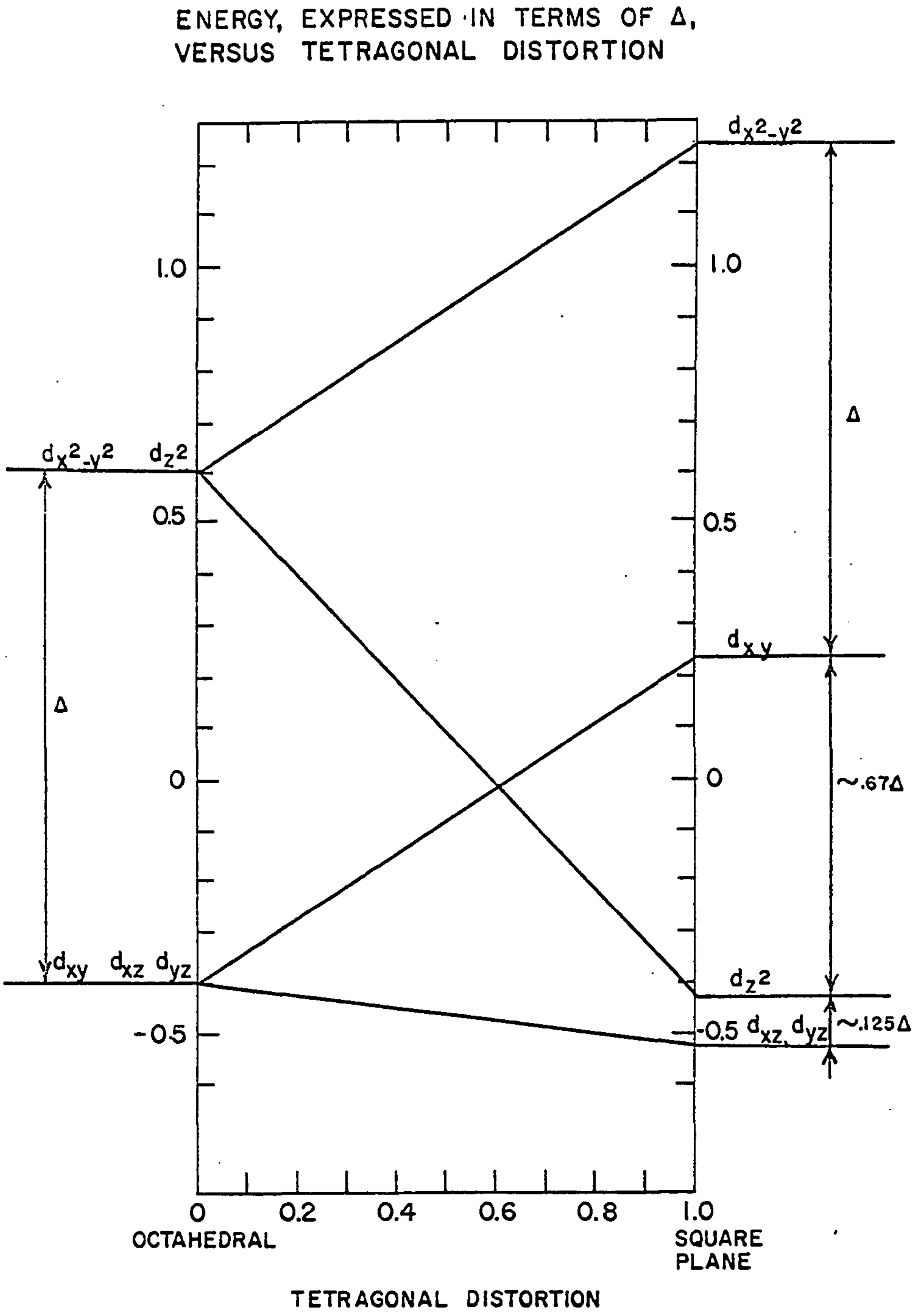


Fig. 15. Crystal field diagram for copper(II)

In the energy level diagram (Fig. 15), the energy level separations for the square planar limit are those given by Cotton and Wilkinson (26). The numbers on the tetragonal distortion axis are relative to assigning a value of zero to a perfect octahedral complex and a value of one to a perfect square planar complex.

2. Electron paramagnetic resonance spectra of $Cu(DMG)_2$

There have been two studies (82, 89) of the EPR spectrum of $Cu(DMG)_2$. Both studies have concluded that $Cu(DMG)_2$ is coordinated to four nitrogen atoms. Wiersema and Windle (89) reported that the degree of covalency for the Cu-N bond was greater when calculated from the copper hyperfine splitting than when calculated from the nitrogen hyperfine splitting. The discrepancy in the covalencies calculated was significantly greater than experimental error.

The EPR study of $Cu(DMG)_2$ by Timerov, Yablokov and Ablov (82) indicated that all four nitrogen atoms coordinated to the copper atom were equivalent. In addition, it was also shown that there was an equal nonzero probability of finding an unpaired electron on the four nitrogen atoms. These investigators also found that the Cu-N bond was covalent and that the nature of this bond remained unchanged in going from the crystalline state into solution. Upon solution, however, these investigators concluded that $Cu(DMG)_2$ did not remain a dimer, but rather became a monomer with the two remaining coordination sites on the copper(II) being occupied by oxygen atoms from two coordinated solvent molecules. The solvents used by these Russian investigators were methanol, dioxane, and water.

3. Solvent extraction of metal-*vic*-dioximes

Solvent extraction studies have shown that $Cu(DMG)_2$ has an affinity for electron-donating ions and molecules. Dyrssen and Hennichs (29) have found that $Cu(DMG)_2$ forms adducts with organic bases such as dodecylamine and quinoline. By solvent extraction techniques these workers have been able to measure the formation constant for interaction of one molecule of quinoline or dodecylamine with one molecule of $Cu(DMG)_2$. The formation constant was of the order of 10^2 indicating that the adduct formation was not exceptionally strong. Dyrssen and Hennichs (29) found that their techniques indicated that $Ni(DMG)_2$ had no tendency toward such adduct formation. In addition, Fleischer (33) has pointed out that the addition of *n*-butylamine enables the quantitative extraction of $Cu(DMG)_2$ from aqueous solution into chloroform. On the other hand, Fleischer (33) noted that *n*-butylamine had little effect on the solubility of $Ni(DMG)_2$ in chloroform. All these solvent extraction observations seemed to indicate that $Cu(DMG)_2$ tended to interact with donor molecules, whereas $Ni(DMG)_2$ showed very little tendency toward such interactions.

4. Solubilities of metal-*vic*-dioximes

Solubility determinations have indicated that $Cu(DMG)_2$ interacted with solvents to a greater extent than did either $Ni(DMG)_2$ or $Ni(EMG)_2$. In water, $Cu(DMG)_2$ is much more soluble than either $Ni(EMG)_2$ or $Ni(DMG)_2$. However, in *n*-heptane $Cu(DMG)_2$ and $Ni(DMG)_2$ are much less soluble than $Ni(EMG)_2$ (1, 33).

It is interesting to note that $Ni(EMG)_2$ is more soluble than $Ni(DMG)_2$ in both *n*-heptane and water. Sharpe and Wakefield (77) have suggested that the greater solubility of $Ni(EMG)_2$ in water compared to the solubility of $Ni(DMG)_2$ was due to the greater stability imparted to the $Ni(DMG)_2$ crystal by the Ni-Ni bond.

Dyrssen and Hennichs (29) have studied the solubility of $Cu(DMG)_2$ as a function of hydroxide ion concentration. They have found that as pH increases the solubility of

$Cu(DMG)_2$ increases. Assuming the species present in an aqueous $Cu(DMG)_2$ solution to be $Cu(DMG)_2 \cdot H_2O$, Dyrssen and Hennichs (29) have calculated the hydrolysis constant for the following reaction:

$$Cu(DMG)_2 \cdot H_2O \overset{K_h}{\rightleftarrows} Cu(DMG)_2 \cdot OH^- + H^+$$

They have found log K_h to be -10.6.

B. Experimental Procedures and Materials

Some of the experimental work pertinent to this section has been described in Part II-B; these descriptions will not be repeated. As in Part II-B equipment, procedures, and chemicals common to any good laboratory will not be described in detail.

1. Instrumentation and apparatus

All spectra were recorded on a Cary Model 14 spectrophotometer. One-cm cells with a region of transmittance from 180 mμ to 1200 mμ were used for most measurements. When low molar absorbtivities and/or low concentrations necessitated the use of thicker cells, 10-cm quartz cells were used.

Spectra of solids were obtained by painting a nujol mull of the solid onto a silica cell window from a broken cell. The painted cell window was then mounted in the sample beam of the spectrophotometer. A similar silica window painted only with the mulling oil was mounted in the reference beam. When necessary a screen was also mounted in the reference beam to compensate for the increased light scattering by the sample.

All pH measurements were made on a battery-powered Beckman Model G pH meter equipped with the appropriate Beckman electrodes. All dilute base solutions were protected from atmospheric carbon dioxide by fitting the containers of such dilute bases with drying tubes filled with "Ascarite". Carbon dioxide was eliminated from all solutions titrated with weak bases by first flushing the solutions with helium or nitrogen for fifteen minutes. The flushing process was continued throughout the titration.

Solutions for conductance measurements were flushed and protected in the same manner as those for pH measurements.

Conductance measurements were made with a Leeds and Northrup No. 4866 conductivity bridge.

2. Solubility measurements

All solubilities were determined at room temperature (approximately 25°C). Saturated solutions of the chelates were prepared by mechanically shaking an excess of the solid with the respective solvents for eight hours or longer. The analysis of the saturated solutions was accomplished by evaporating the solvent from a measured aliquot and dissolving the residue in a 1 M aqueous HNO_3 solution saturated with either DMG or EMG. The solutions were diluted to a measured volume with the final acid concentration being 0.2 M. Standards were treated in a similar manner. The analysis was carried out with the aid of a Perkin-Elmer Model 303 Atomic Absorption Spectrophotometer. Some of the solubilities were also determined by other investigators (1, 33); and within experimental error, the results of this study agreed well with those of other investigations.

3. Solvents

Chloroform (cut-off at 250 mμ) and benzene (cut-off at 280 mμ) were described in Part II-B.

Absolute ethanol (cut-off at 230 mμ) was a product of Commercial Solvents.

Acetonitrile was Eastman "spectro grade" (cut-off at 220 mμ).

4. Analysis

The concentration of *n*-butylamine in the various solvents was determined by nonaqueous titration using a standardized solution of perchloric acid in acetic acid as a titrant. Crystal violet was the indicator used. The procedure presented by Fritz and Hammond (38, p. 265-266) was followed.

C. Experimental Results

The actual gathering of data concerning the solution chemistry of the metal-*vic*-dioximes encompassed several areas. None of these areas was meant to be a study in depth. The object was to gain some knowledge concerning the nature of the difference of $Cu(DMG)_2$ and $Ni(DMG)_2$ in solution. The major areas from which data were obtained were the ultraviolet and visible spectra, pH measurements, conductance measurements, and solubility determinations in several solvents.

1. Solubility determinations

The solubilities of $Cu(DMG)_2$, $Ni(DMG)_2$, and $Ni(EMG)_2$ in water, acetonitrile, chloroform, benzene, absolute ethanol, and *n*-heptane are listed in Table 13. Two points from Table 13 should be remembered for the later discussion of these results. First of all the trend in the solubility of $Cu(DMG)_2$ relative to the nickel chelates should be noted. Secondly, it should be pointed out that for each solvent studied $Ni(EMG)_2$ is significantly more soluble than $Ni(DMG)_2$.

Table 13. Solubilities of some metal-vic-dioximes in various solvents

	pS where S = moles/liter		
Solvent	$Cu(DMG)_2$	$Ni(DMG)_2$	$Ni(EMG)_2$
Water	2.19	5.98[a]	5.56[c]
Chloroform	3.03	3.34	1.65
Benzene	4.12	4.06[b]	2.53
Acetonitrile	2.84	4.16[b]	3.14
Absolute ethanol	2.36	4.62[b]	3.88
n-heptane	6.74[a]	6.60[a]	5.91[c]

[a] Reference 33.
[b] By spectrophotometry.
[c] Reference 1.

2. Ultraviolet and visible spectra

The highest energy charge transfer band for $Cu(DMG)_2$ shifted significantly as the solvent media was varied. (See Fig. 16). The variations in the wavelength and frequency at which this band occurs in different solvents are listed in Table 14. The molar absorptivity of this band increased when increasing amounts of n-butylamine were added to a $Cu(DMG)_2$ solution. This effect is illustrated in Fig. 17.

Table 14. Location of highest energy metal to ligand charge transfer band in $Cu(DMG)_2$

Solvent	Wavelength (mμ)	Frequency (cm^{-1})
H_2O	267	37,500
C_2H_5OH (absolute)	276	36,300
CH_3CN	279	35,800
$CHCl_3$	281	35,600
C_6H_6	285	35,100

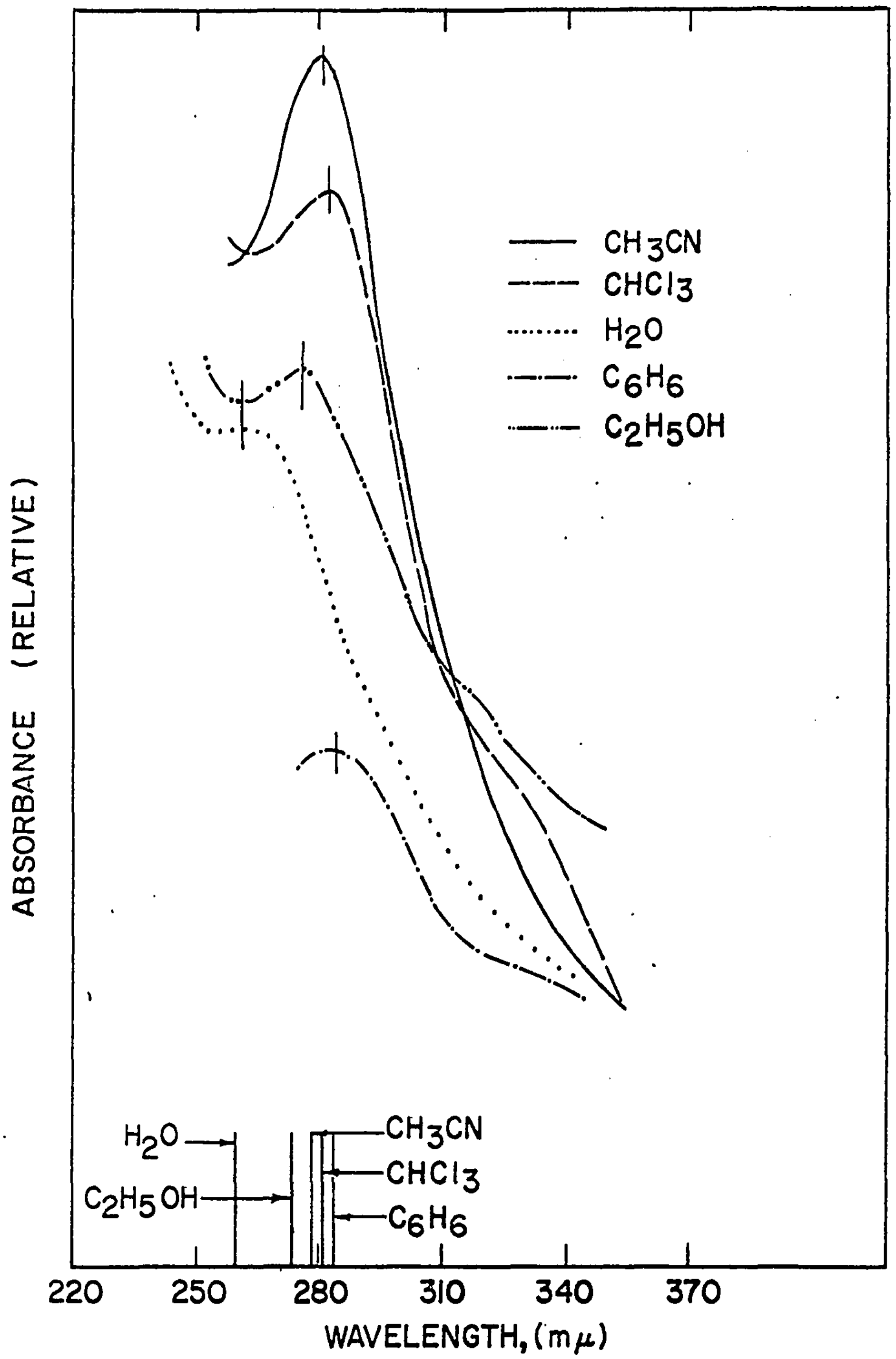


Fig. 16. Highest energy charge transfer band of $Cu(DMG)_2$ in various solvents

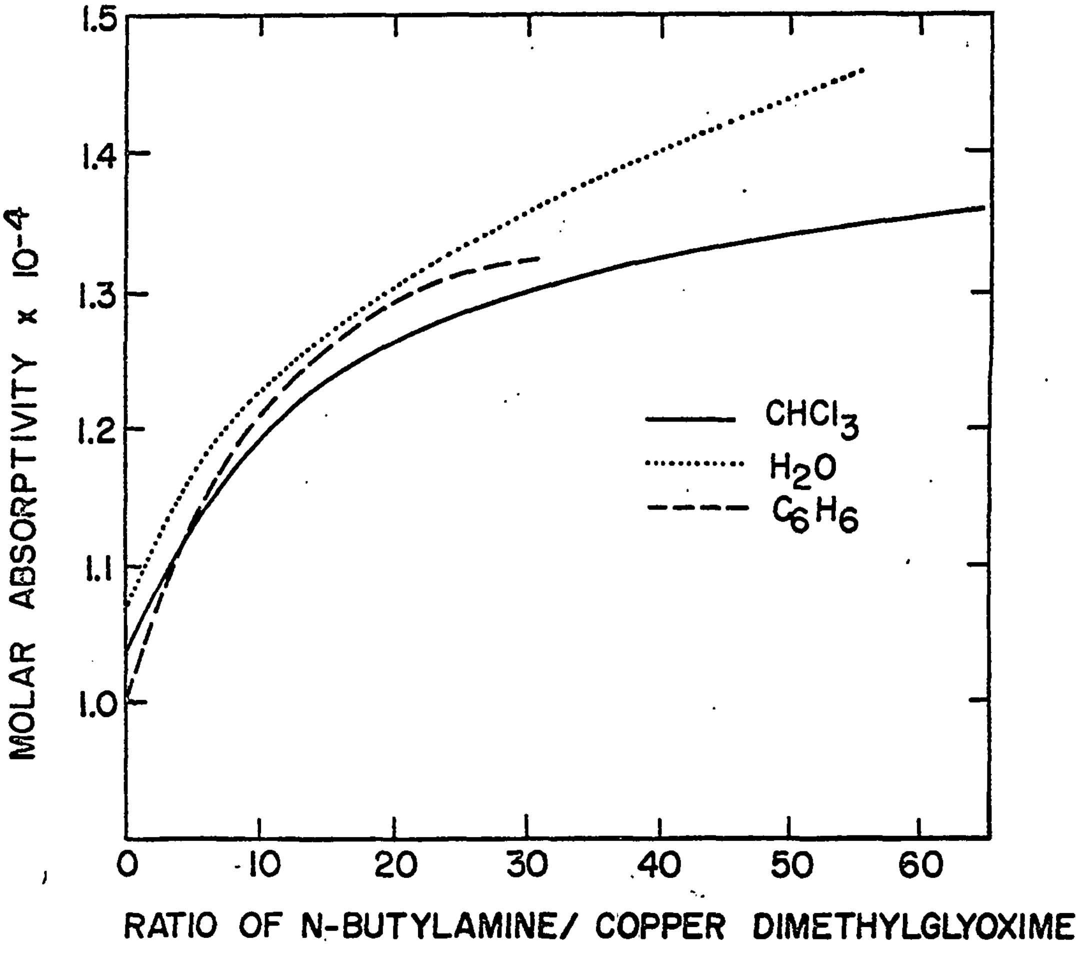


Fig. 17. Change in the molar absorptivity of the highest energy charge transfer band of $Cu(DMG)_2$ as a function of n-butylamine concentration

The visible spectrum of $Cu(DMG)_2$ is also affected by a variation in solvent. An attempt was made to resolve the visible spectra in Fig. 18 by considering each spectrum to consist of a linear combination of Gaussian curves. The resolution was accomplished by trial and error starting with the highest energy ultraviolet band and working down into the visible spectrum (48, p. 101). Counting the band characteristic of the glyoxime radical found near 44,000 cm^{-1}, the resolved spectra contained seven bands between 10,000 and 45,000 cm^{-1}. On the low frequency side of the charge transfer band described previously, two additional bands with molar absorptivities on the order of 10^3 were resolved. Based on their high molar absorptivities, these bands evidently arose from allowed transitions. Finally, three bands with molar absorptivities on the order of 10^2 were resolved at the visible end of the spectra. These three bands probably correspond to the three _d_-_d_ transitions predicted by crystal field theory for copper(II) in a tetragonally distorted field (26, p. 565).

Figs. 19, 20, 21, and 22 each contain the experimentally determined spectrum, the calculated spectrum, and the resolved bands for $Cu(DMG)_2$ in a given solvent.

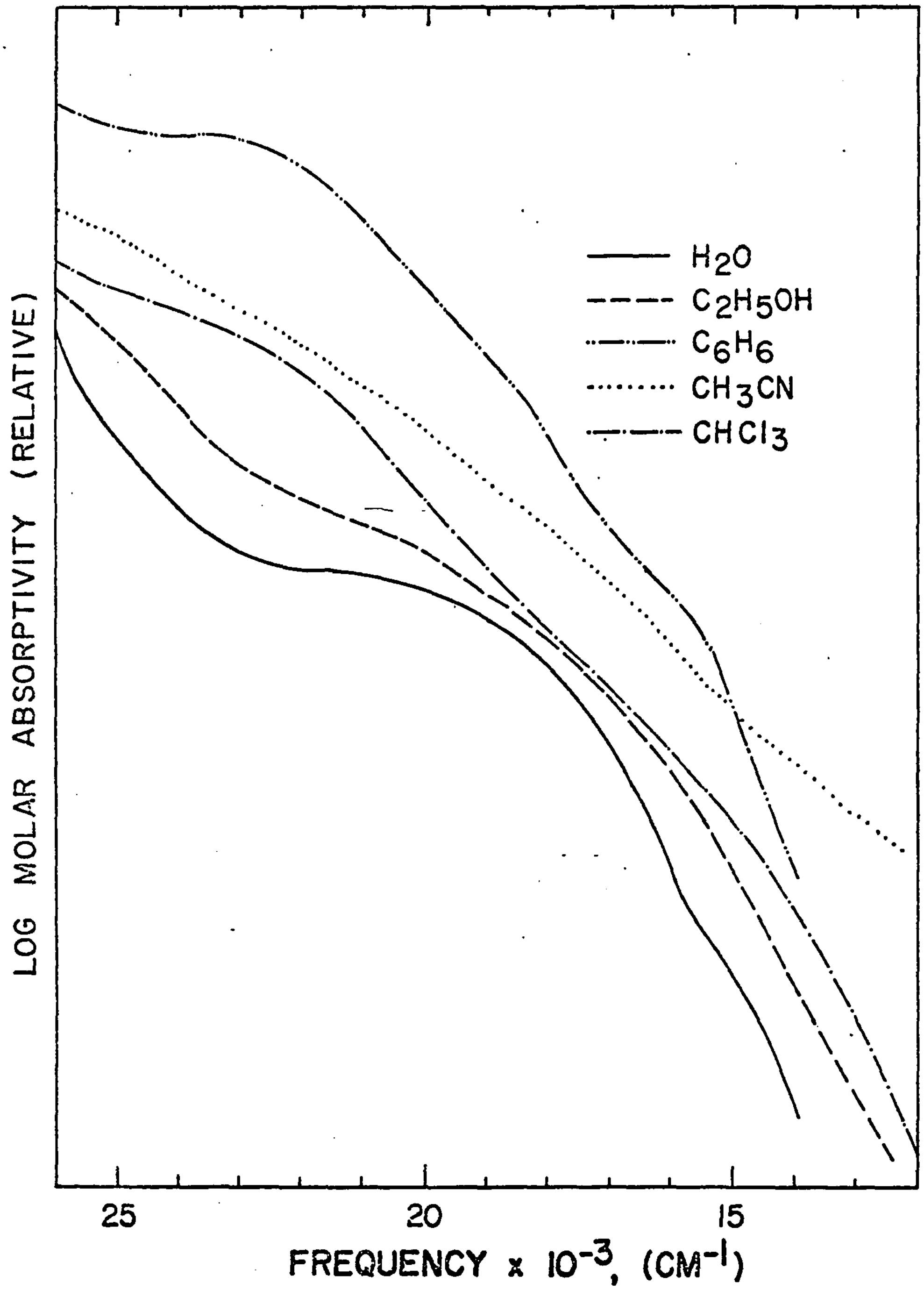


Fig. 18. Visible spectra of Cu(DMG)$_2$ in different solvents

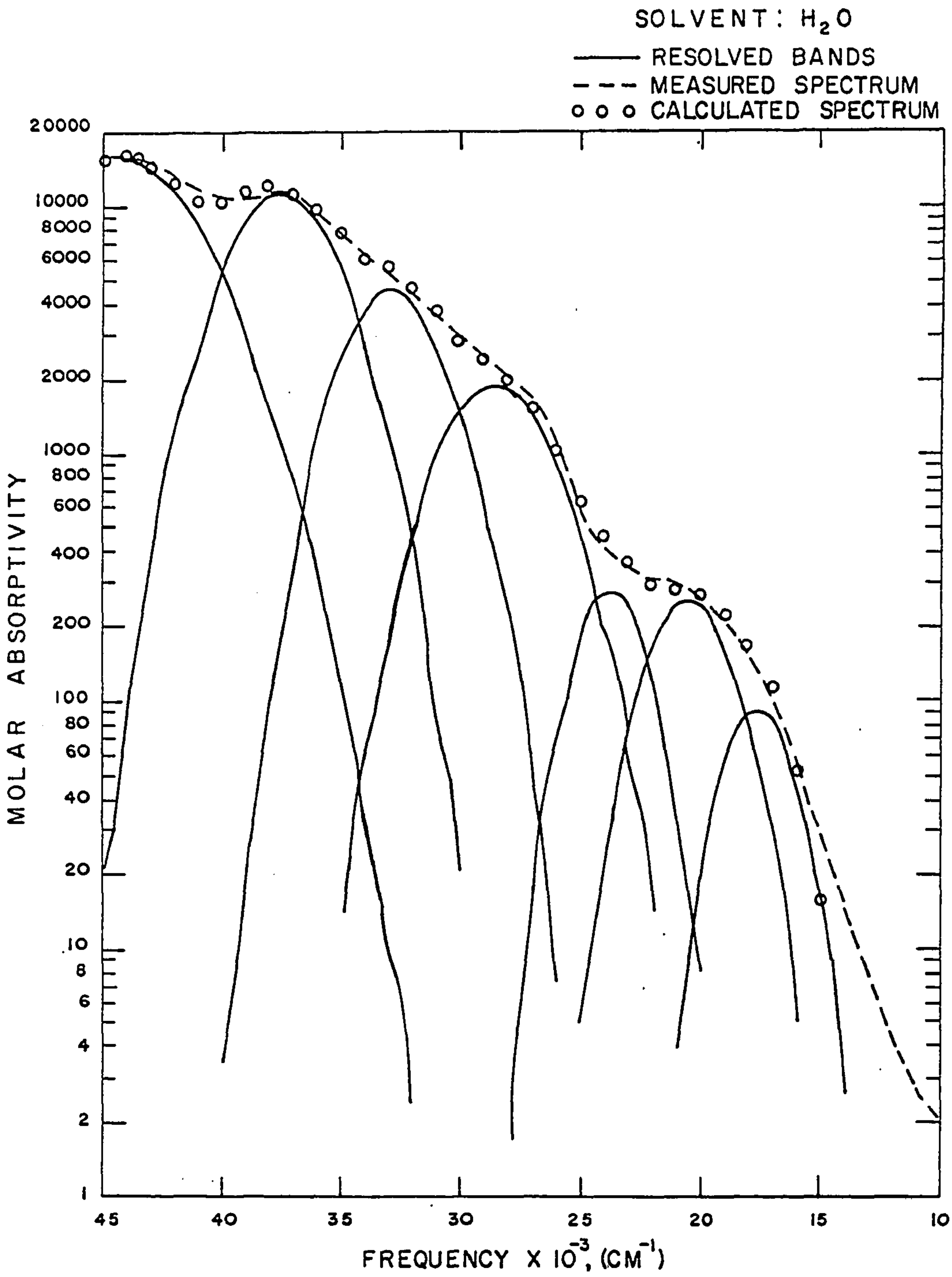


Fig. 19. Resolved spectrum of $Cu(DMG)_2$ in water

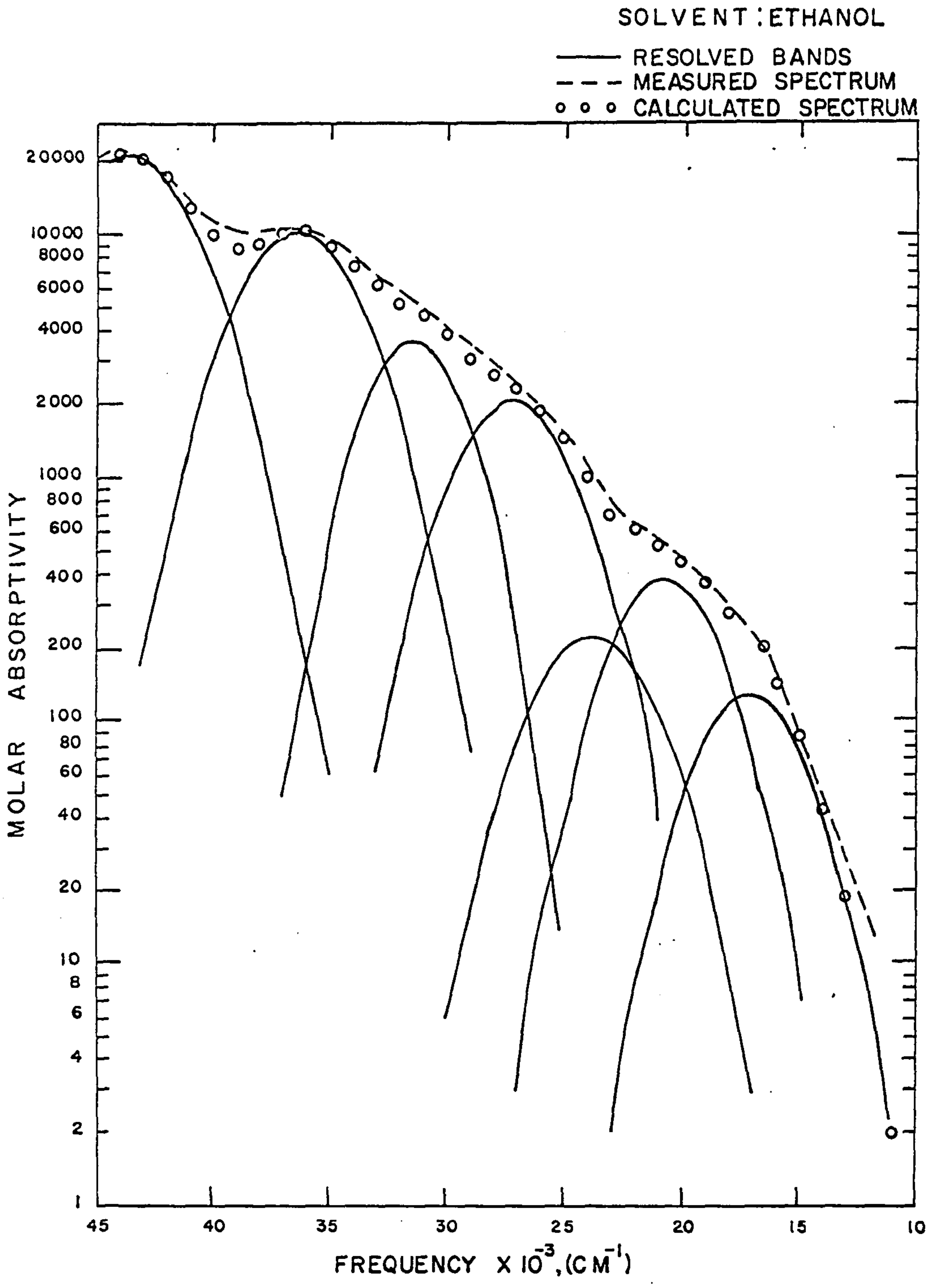


Fig. 20. Resolved spectrum of $Cu(DMG)_2$ in absolute ethanol

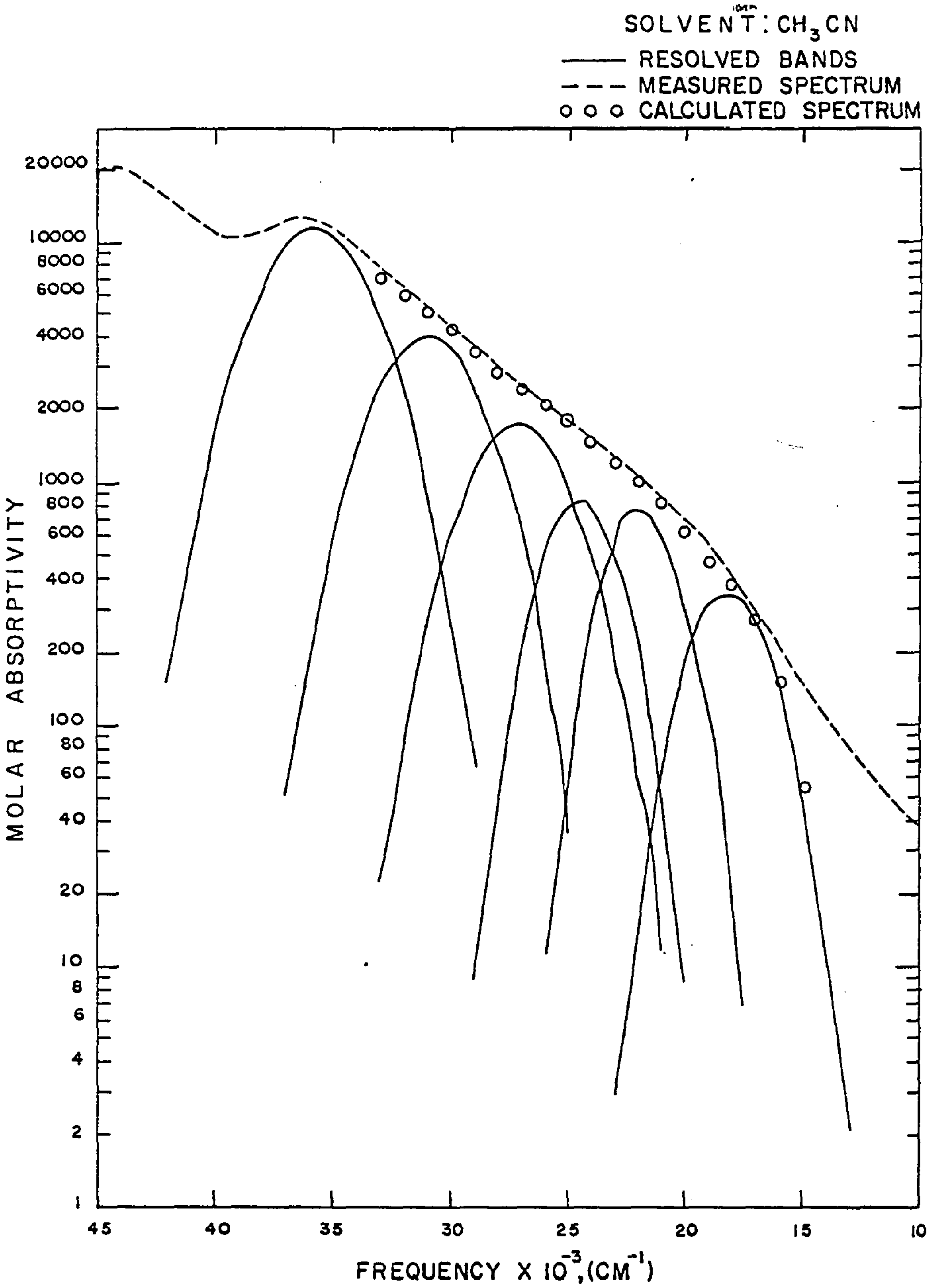


Fig. 21. Resolved spectrum of $Cu(DMG)_2$ in CH_3CN

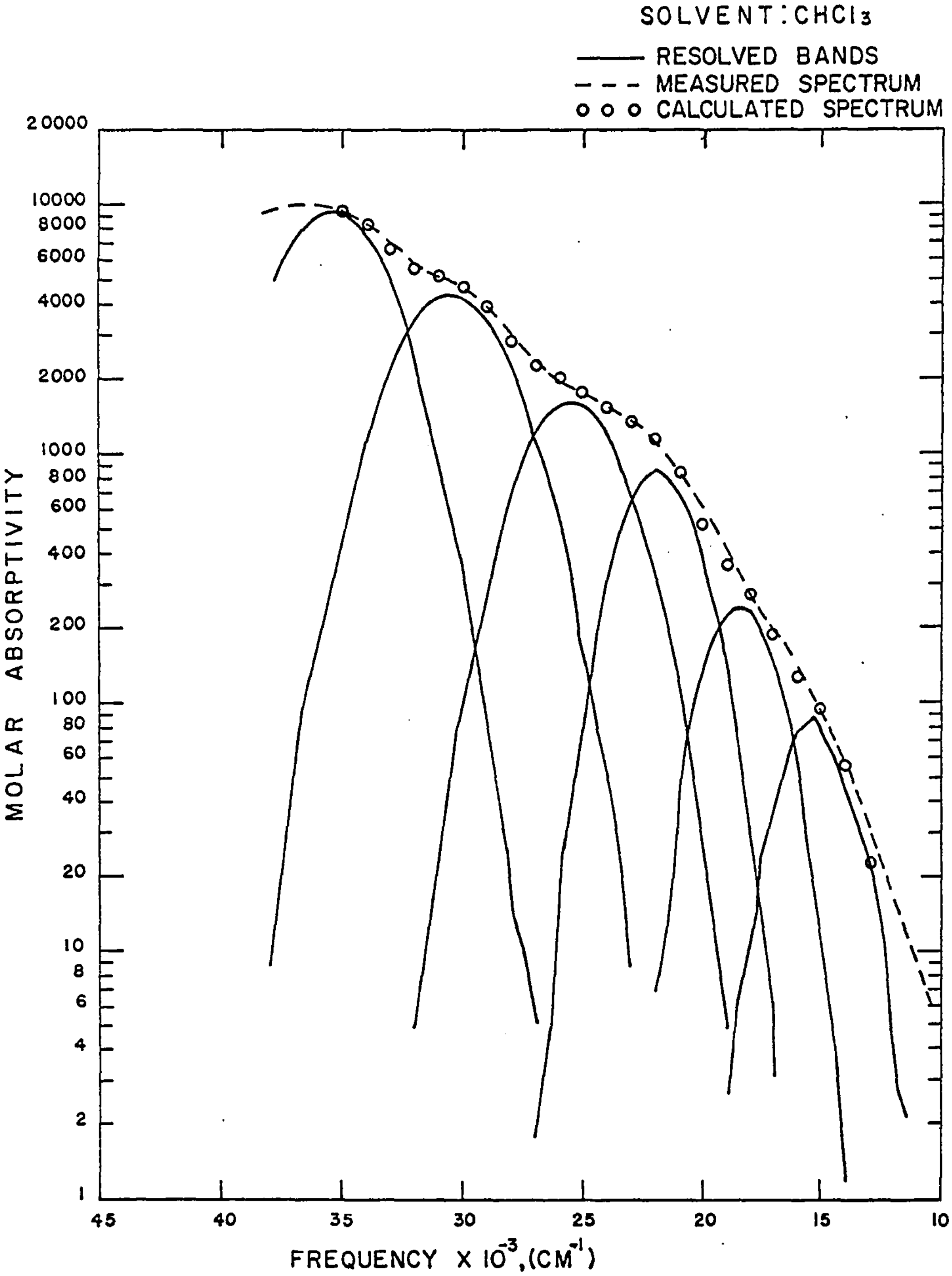


Fig. 22. Resolved spectrum of $Cu(DMG)_2$ in $CHCl_3$

The energies of the resolved visible bonds did not fit the energy level diagram (Fig. 15) as well as the fit obtained by other workers (12) for the solvent effect on copper acetylacetone. The reason for this poor fit may have been due in part to error in resolving the visible bands. Because the low intensity bands are just a shoulder on the much more intense charge transfer bands, a small error in resolving the charge transfer bands could introduce a significant error into the resolution of the low intensity bands. A second and more probable reason for the poor fit is that the simple crystal field picture may break down for the metal-*vic*-dioximes due to π-bonding effects (28). Nevertheless, the data obtained did indicate the following solvent sequence arranged in order of strength of interaction with $Cu(DMG)_2$:

$$H_2O >> C_2H_5OH \overline{>} CH_3CN > CHCl_3 > C_6H_6.$$

The spectra of $Ni(DMG)_2$ and $Ni(EMG)_2$ in Fig. 23 were not significantly affected by solvent variation or even by the presence of *n*-butylamine in a given solvent. Neither the molar absorptivity nor the location of any of the maxima changed when the mole ratio of *n*-butylamine to chelate was 500 to 1 for $Ni(DMG)_2$ or in excess of 100 to 1 for $Ni(EMG)_2$.

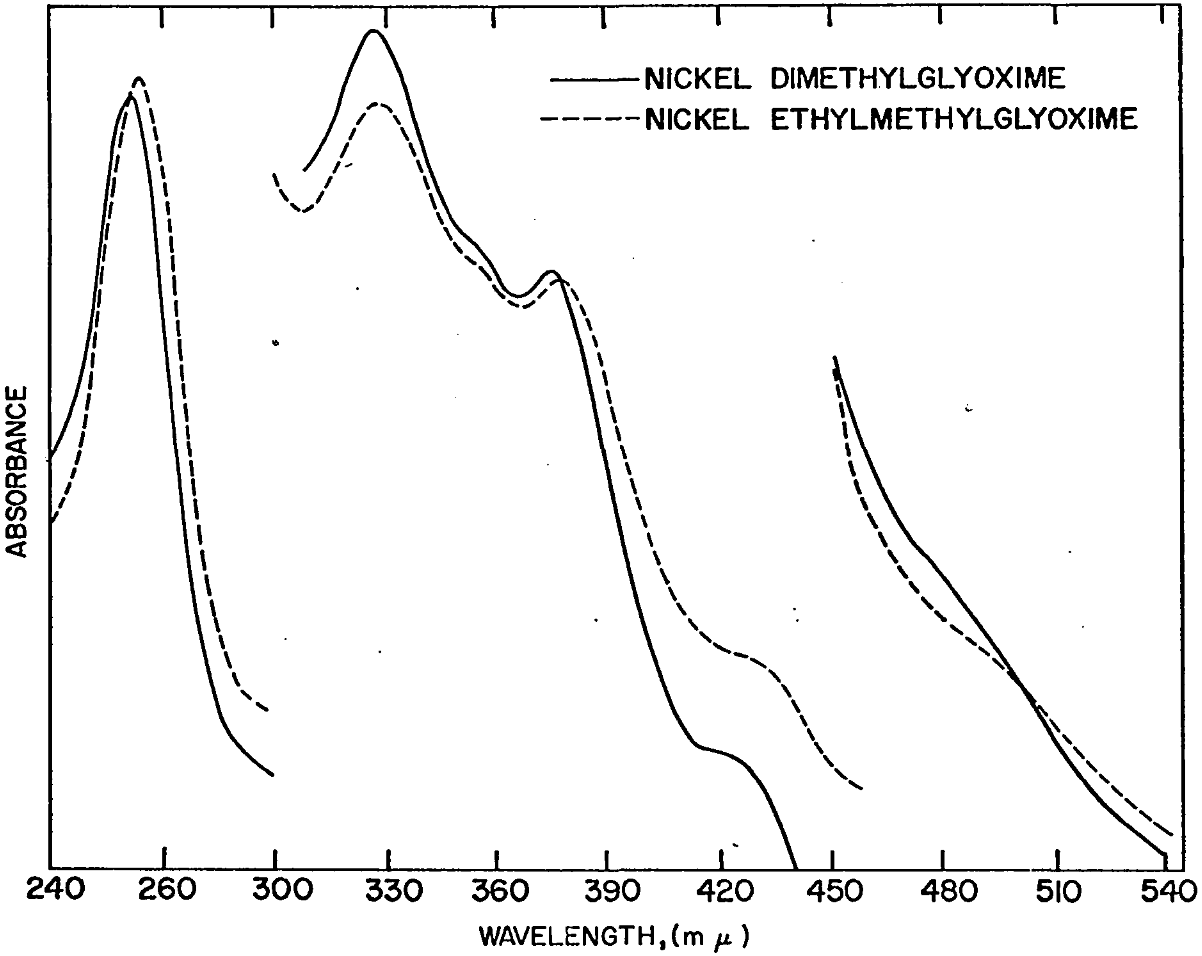


Fig. 23. Spectra of $Ni(DMG)_2$ and $Ni(EMG)_2$ in chloroform solution

(The effect of higher concentrations of n-butylamine was not determined for either chelate.)

3. Miscellaneous results

Since Dyrssen and Hennichs (29) had shown that $Cu(DMG)_2$ did form adducts with the hydroxide ion, it was thought that following the pH of an aqueous solution of $Cu(DMG)_2$ as it was titrated with dilute sodium hydroxide might reveal the number of hydroxide ions reacting with each molecule of $Cu(DMG)_2$. The solid curve in Fig. 24 represents such a titration. The broken curve in Fig. 24 represents the titration of water with the same base. The difference in these two curves would represent the amount of hydroxide ion that was tied up in some manner so that the glass electrode did not respond to its presence. Thus, $Cu(DMG)_2$ did act as a weak acid. However, there were no breaks in the pH titration curve to indicate the number of hydroxide ions reacting with $Cu(DMG)_2$.

Conductance studies of aqueous $Cu(DMG)_2$ solutions yielded much the same information as the pH studies. The presence of $Cu(DMG)_2$ reduced the conductance expected for a given concentration of hydroxide ion. However, no conclusions could be made concerning the stoichiometry of the

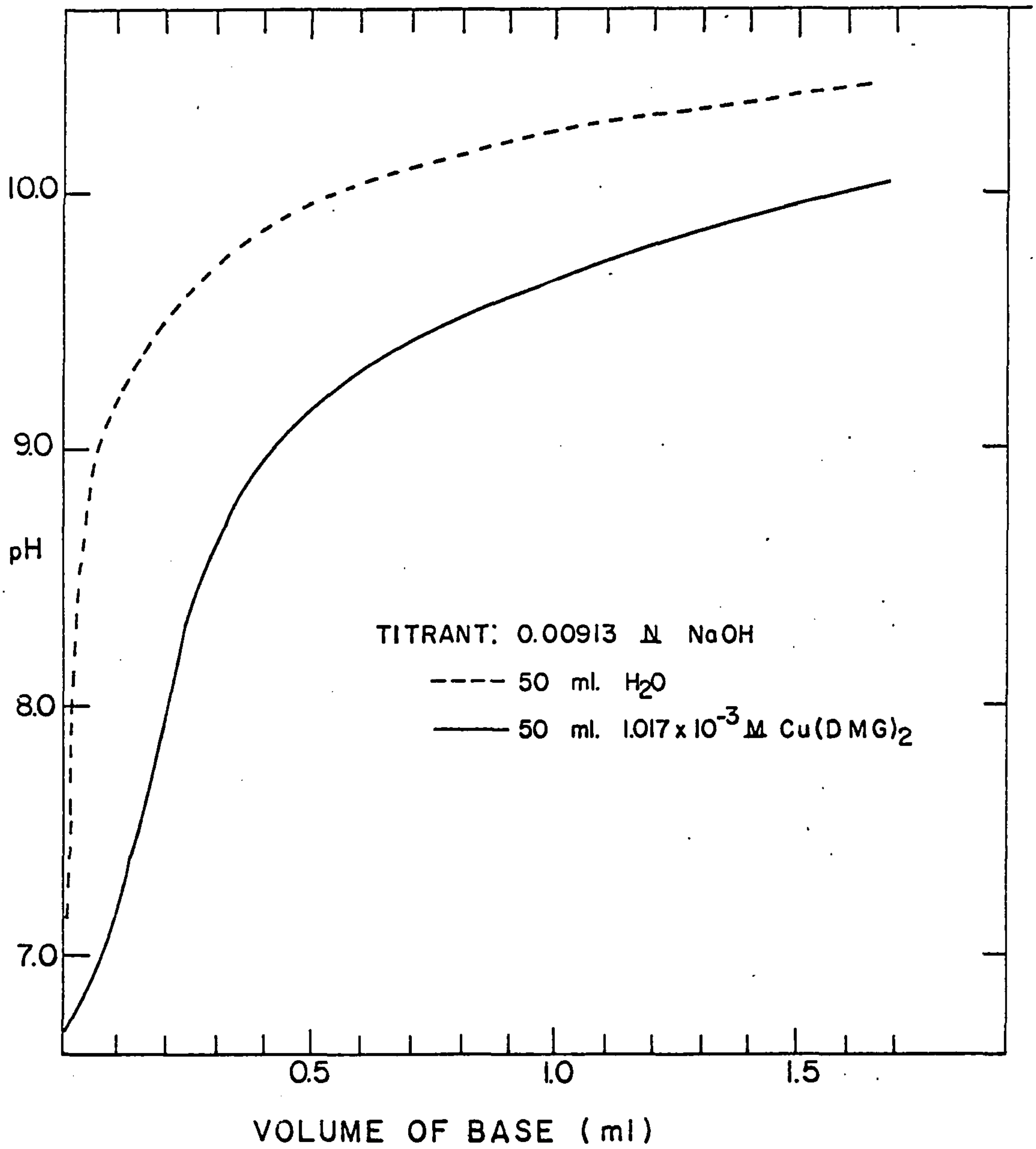


Fig. 24. Titration of aqueous solution of $Cu(DMG)_2$ with dilute base

interaction between $Cu(DMG)_2$ and the hydroxide ion. Nevertheless, the conductance studies showed that $Cu(DMG)_2$ behaved as a weak electrolyte in aqueous solution. The conductance curve for $Cu(DMG)_2$ in Fig. 25 was characteristic of a weak electrolyte. Such a curve was to be expected if the hydrolysis of $Cu(DMG)_2$ claimed by Dyrssen and Hennichs (29) did occur.

Based on the observations of Fleischer (33) _n_-butylamine was expected to substantially increase the solubility of $Cu(DMG)_2$ in chloroform. It was found that the presence of _n_-butylamine in chloroform did increase the solubility of $Cu(DMG)_2$ in a fairly linear manner. As is illustrated in Fig. 26, every mole of _n_-butylamine added to a chloroform solution allowed an additional 0.17 mole of $Cu(DMG)_2$ to dissolve in the solution.

If the solvent was allowed to evaporate from the mixture of $Cu(DMG)_2$, _n_-butylamine, and chloroform, a finely divided brown solid was obtained. When this solid was dried at room temperature, the molecular weight based on one copper atom per molecule corresponded to the molecular weight of $Cu(DMG)_2$ plus one _n_-butylamine molecule. By drying this product in an oven at 110°C for two hours, the molecular

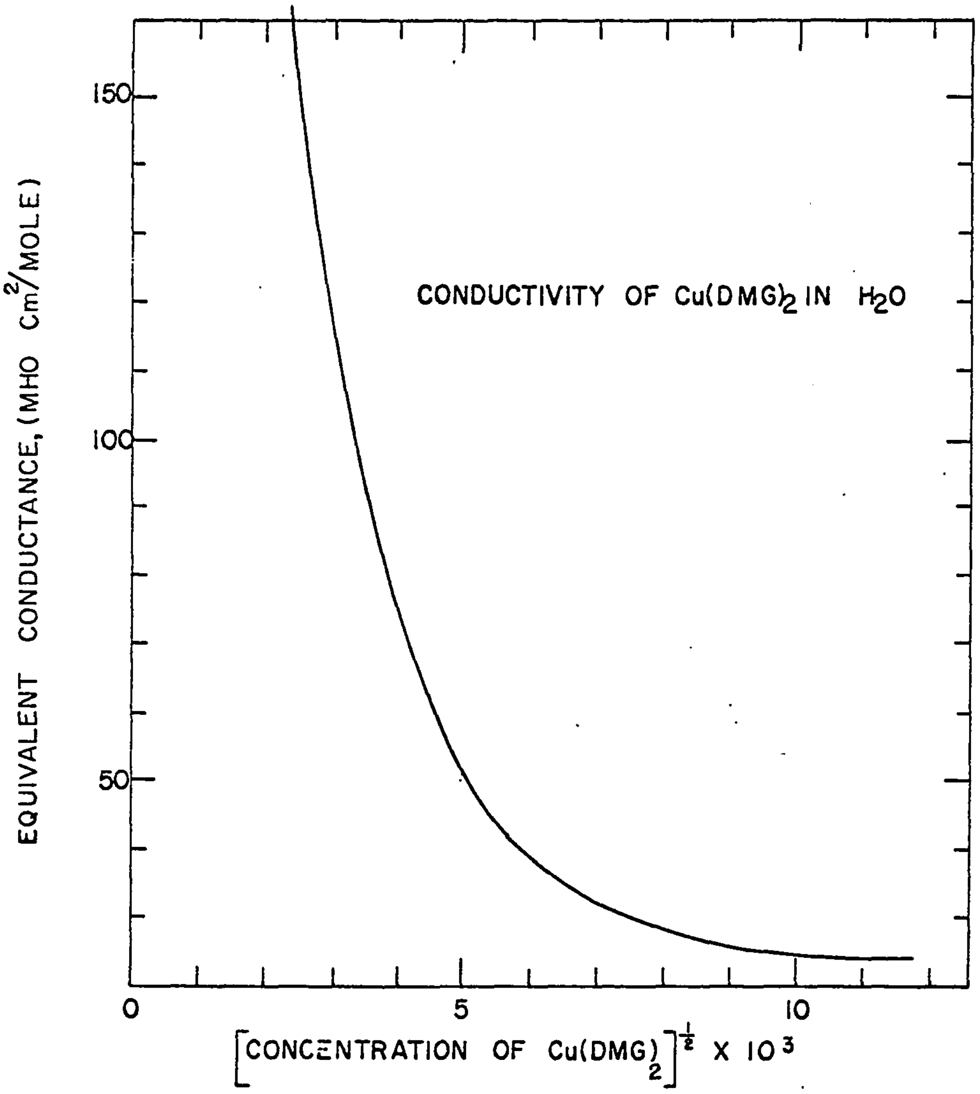


Fig. 25. Conductivity curve for $Cu(DMG)_2$ in water

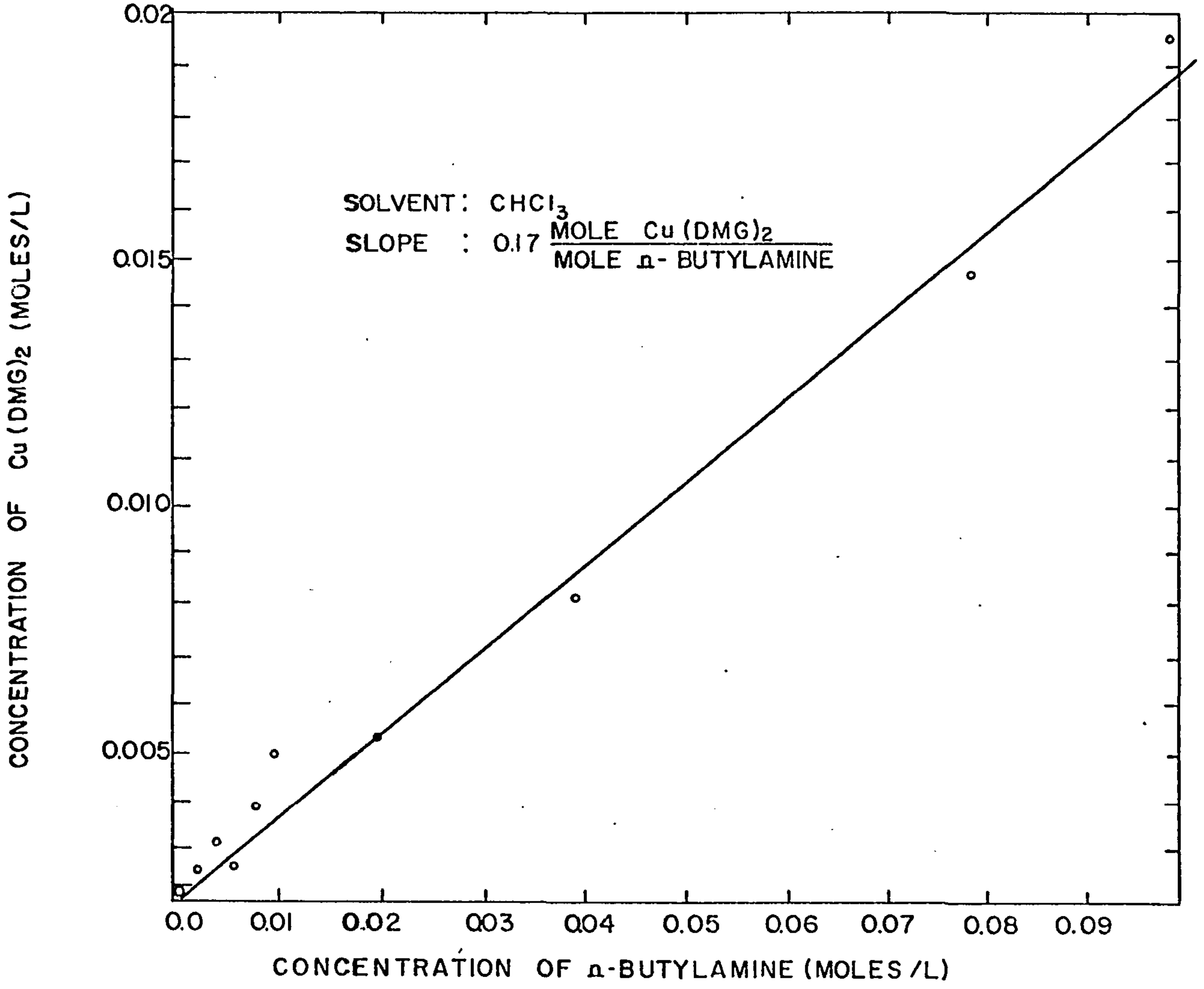


Fig. 26. Effect of n-butylamine on concentration of $Cu(DMG)_2$ in $CHCl_3$

weight was reduced to about that of Cu(DMG)$_2$ alone. However, as the reader can see in Table 15, after oven drying the molecular weight based on one copper atom per molecule was slightly high for Cu(DMG)$_2$.

Table 15. Molecular weight of Cu(DMG)$_2$ recrystallized from a solution of chloroform and n-butylamine

Sample number	Dried at room temperature	Dried at 110°C
1	374.5	307.1
2	369.6	309.7
3	373.9	302.8
4	373.8	____
Average	372.9	306.5

Molecular weight of Cu(DMG)$_2$ + n-butylamine = 366.9

Molecular weight of Cu(DMG)$_2$ = 293.8

The infrared spectrum of the product obtained upon the evaporation of the solution of Cu(DMG)$_2$, n-butylamine, and chloroform indicated that the Cu(DMG)$_2$ molecular structure was preserved. The spectrum was identical to that of crystalline Cu(DMG)$_2$ except for additional bands characteristic of _n_-butylamine.

D. Discussion and Conclusions

An explanation is offered for the behavior of the ultraviolet spectrum of Cu(DMG)$_2$ in different solvents. The characteristics of the visible spectrum of Cu(DMG)$_2$ are discussed. In addition, some comment is made concerning the effect of electron donor molecules or ions on Cu(DMG)$_2$. Where it is pertinent, the behavior of Ni(DMG)$_2$ and Ni(EMG)$_2$ is compared to the behavior of Cu(DMG)$_2$ for the given situation.

1. Ultraviolet spectrum of Cu(DMG)$_2$

Burger, Ruff, and Ruff (22) have assigned the highest energy charge transfer band (Fig. 16) in Cu(DMG)$_2$ as a metal to ligand charge transfer. Data from this investigation support this assignment. The molar absorptivity of the band increased upon the addition of _n_-butylamine (Fig. 17). If the _n_-butylamine is considered to co-ordinate with the copper, it can be assumed that the electron density on the copper is increased because the _n_-butylamine should be a better donor than any of the solvents listed in Fig. 17.

With the increased electron density on the copper atom, the probability of a metal to ligand charge transfer becomes greater (57); therefore, the molar absorptivity of the band increases. Additional evidence that a metal to ligand charge transfer takes place is the shift of a C=N vibration from 1587 cm^{-1} in solid $Cu(DMG)_2$ to 1594 cm^{-1} for a saturated solution of $Cu(DMG)_2$ in chloroform which is also 0.1 $\underline{M}$ in $\underline{n}$-butylamine. The small frequency increase indicates a slightly stronger C=N bond, which evidently results from a small increase in electron density on the nitrogen atom due to the metal to ligand charge transfer.

Concerning the variation in the frequency of the maxima of the highest energy charge transfer band in $Cu(DMG)_2$ (Table 14), it is interesting to note the almost linear correlation between the energy of the charge transfer band and the solubility of $Cu(DMG)_2$ in a given solvent. (See Fig. 27).

The explanation for the variation in the frequency of this charge transfer band due to different solvents is apparently similar to that for the pyridine-iodine complex in solvents of increasing polarity (68). The more polar solvent surrounding a molecule in solution causes the

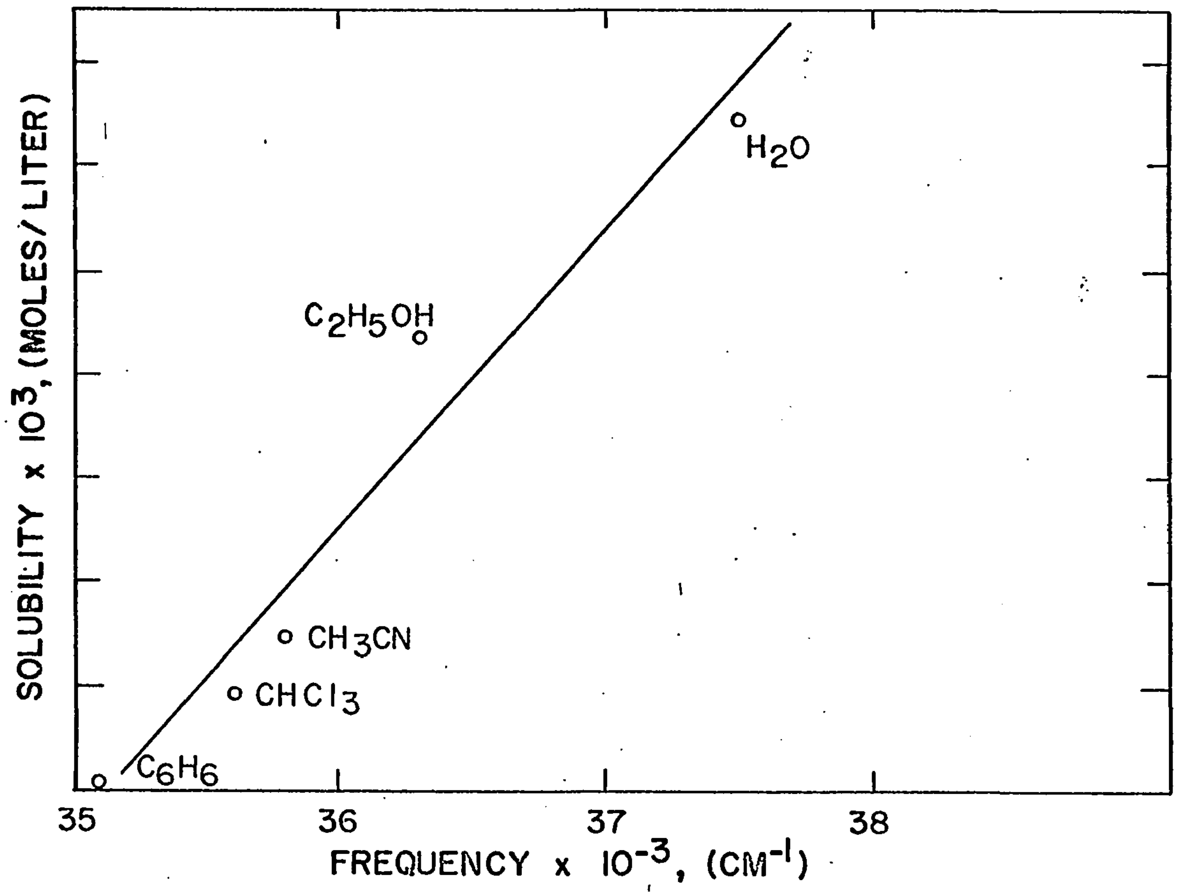
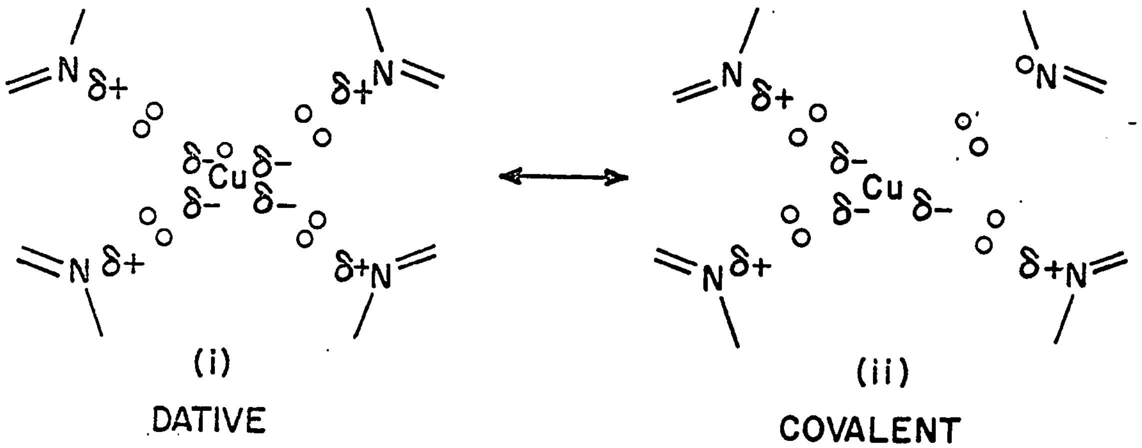


Fig. 27. Frequency of the highest energy charge transfer band of $Cu(DMG)_2$ as a function of the solubility of $Cu(DMG)_2$ in various solvents

molecule to become more polar. The polarizable portions, therefore, have a greater tendency to retain their charge in a more polar solvent. Now, in the case of $Cu(DMG)_2$, it has been shown (82) that the Cu-N bonds are covalent and that there is an equal nonzero probability of finding an unpaired electron on the four nitrogen atoms. Therefore, the Cu-N bonds can be thought of as some hybrid of structures illustrated in Fig. 28. Fig. 28(i) represents the Cu-N bonds as tending toward dative bonds with the nitrogen atoms donating both electrons. These dative bonds are then slightly polar with the nitrogen atoms being electron deficient and the copper atom having some excess negative charge. On the other hand, Fig. 28(ii) represents the situation where the unpaired *d*-electron of the Cu(II) enters into a covalent bond with the net effect being the reduction in the polarity of the Cu-N bonds and the presence of a single unpaired electron on the nitrogen atom. Fig. 29 illustrates the increase in energy of the charge transfer band as the dipole moment of the solvent increases. Because the metal to ligand charge transfer requires greater energy as the solvent becomes more polar, it would appear that the structure represented in Fig. 28(ii) becomes slightly more



(i)
DATIVE

(ii)
COVALENT

Fig. 28. Possible representations for the Cu-N bonds in $Cu(DMG)_2$

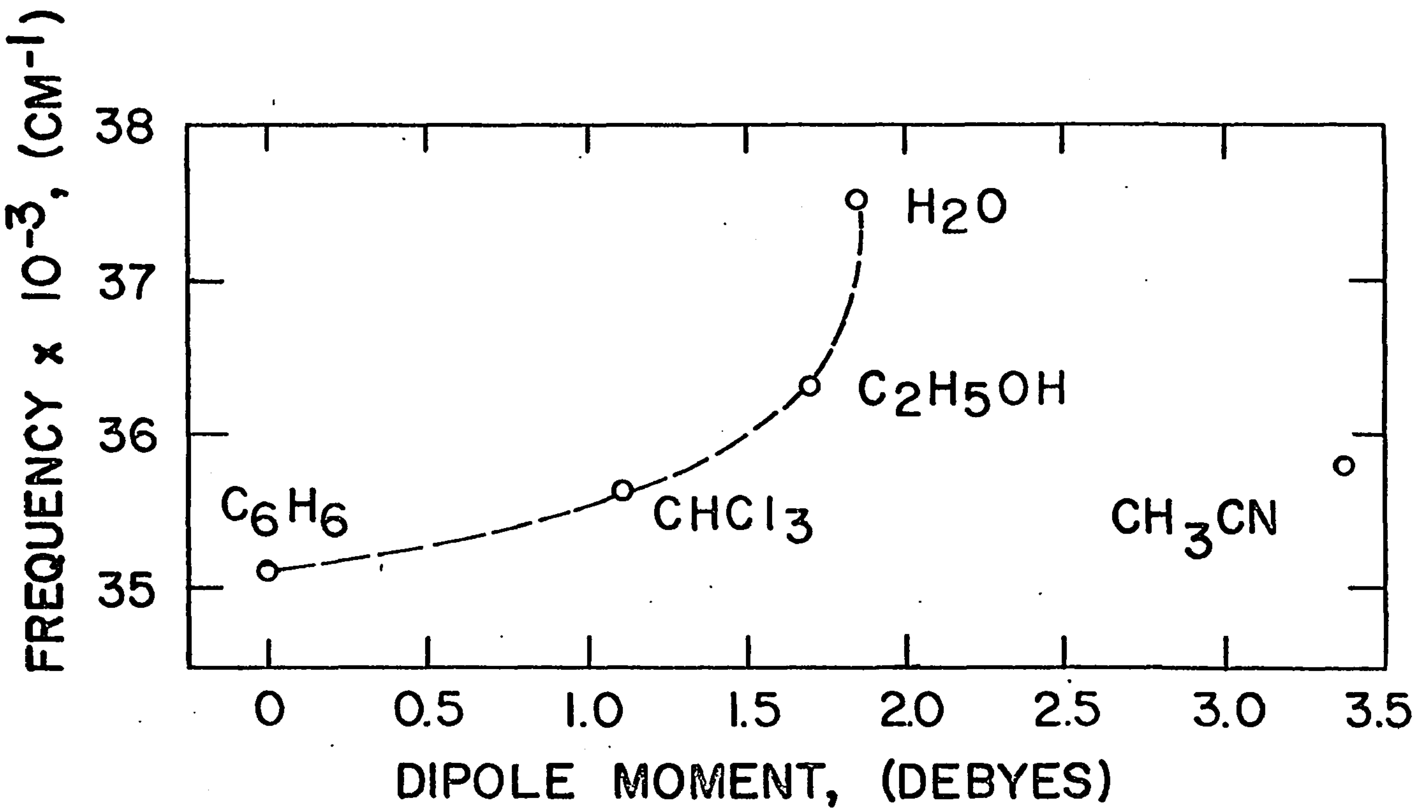


Fig. 29. Variation in the frequency of the highest energy metal to ligand charge transfer band of $Cu(DMG)_2$ as a function of the dipole moment of the solvent

important in the charge transfer excited state than in the ground state. However, the structure in Fig. 28(ii) should be predominant in both the ground state and the excited state because there are four possible resonances for this representation of the Cu-N bond. This representation would also indicate that the Cu-N bond was always predominantly of a dative character; because copper(II) has only one unpaired electron available for covalent bonding resulting in a minimum of one normal covalent bond and three dative bonds for the extreme normal covalent case [Fig. 28(ii)]. Thus, this interpretation of the charge transfer spectra indicated that while the Cu-N bonds remained covalent in all solvents, the amount of dative covalent character varied slightly with solvent media.

The model proposed for the Cu-N bond (Fig. 28) is consistent with the idea of a metal to ligand charge transfer and with the EPR data. In going from the structure in Fig. 28(i) to the structure in Fig. 28(ii) a metal to ligand charge transfer is taking place; and the interpretation of the charge transfer spectra revealed that the structure in Fig. 28(ii) should be more predominant in the excited state than in the ground state.

The second structure in Fig. 28 puts a single unpaired electron on one of the nitrogen atoms. The three other resonances of this structure would in turn put a single unpaired electron on each of the other three nitrogen atoms. Such a situation is in very good agreement with the EPR studies of Timerov, Yablokov, and Ablov (82) who stated that there was an equal and nonzero probability of finding an unpaired electron on the four nitrogen atoms. The unpaired electron on the nitrogen atom would also be compatible with the EPR work of Wiersema and Windle (89) who calculated a greater degree of covalency for the Cu-N bond from the copper hyperfine splitting than from the nitrogen hyperfine splitting.

The energy of the charge transfer bands of $Ni(DMG)_2$ and $Ni(EMG)_2$ was independent of solvent media. On the basis of the explanation proposed for the shift of the $Cu(DMG)_2$ charge transfer bands due to solvent, the bands of the nickel chelates would not be expected to shift; because the nickel(II) would have its eight _d_-electrons paired. Because nickel(II), unlike copper(II) does not have a labile unpaired _d_-electron, which could participate in Ni-N bonding, the Ni-N bonds should be represented by the dative bond structure

[Fig. 28(i)]. The structure with the normal covalent bond [Fig. 28(ii)] is expected to assume little importance for the nickel chelates. Consequently, one would not expect the solvent effect observed for $Cu(DMG)_2$ to occur for $Ni(DMG)_2$ or $Ni(EMG)_2$.

2. Visible spectra

It seems safe to say that the variations of the visible spectrum of $Cu(DMG)_2$ with solvent do indicate that different solvents interact with $Cu(DMG)_2$ to varying degrees. The trend for the extent of solvent interaction determined from the resolution of the visible spectra is logical. Of the solvents studied water was indicated to interact the most with $Cu(DMG)_2$ in solution; and this was the solvent in which $Cu(DMG)_2$ was most soluble. Similar statements could be made for each solvent studied. In fact, the solvent sequence arranged in order of strength of interaction with $Cu(DMG)_2$, which was presented earlier in this manuscript, could also have been solvent sequence arranged in order of solubility of $Cu(DMG)_2$. Thus, the resolution of the visible spectrum of $Cu(DMG)_2$ did yield the results generally expected even though the fitting of the resolved bands to the energy level diagram was not completely successful.

Neither the ultraviolet nor the visible spectra of $Ni(DMG)_2$ and $Ni(EMG)_2$ were affected by variation in solvent media. Even the addition of n-butylamine to the solutions of these nickel chelates did not cause observable changes in the spectra. Apparently the two nickel chelates have practically no tendency to undergo significant solvation or even to interact with a fairly good donor molecule such as n-butylamine.

3. Solubilities

The order of increasing solubility for the three chelates in an inert solvent such as n-heptane is: $Ni(EMG)_2 > Ni(DMG)_2 \overline{>} Cu(DMG)_2$. (See Table 13.) This order is also reflected in the enthalpies of solution (73) of the three chelates in n-heptane: $Ni(EMG)_2$ (5.8 kcal/mole), $Ni(DMG)_2$ (14.8 kcal/mole), and $Cu(DMG)_2$ (16.6 kcal/mole). Therefore, in order for $Cu(DMG)_2$ to be more soluble than the nickel chelates, it must interact with the solvent in some manner so as to overcome its greater enthalpy of solution in an inert solvent.

There appeared to be plenty of evidence for the interaction of $Cu(DMG)_2$ with non-inert solvents and donor molecules and ions. The behavior of the visible spectra of

$Cu(DMG)_2$ in different solvents indicated that $Cu(DMG)_2$ did interact with most solvents. In addition, the slower than expected rise in the pH upon addition of dilute sodium hydroxide to $Cu(DMG)_2$ solution showed that the hydroxide ion was being tied up in some manner. The conductivity data for $Cu(DMG)_2$ in aqueous solution indicated that this chelate was behaving as a weak electrolyte, evidently undergoing the hydrolysis described by Dyrssen and Hennichs (29). The increase in the solubility of $Cu(DMG)_2$ in chloroform due to the presence of n-butylamine yielded direct evidence for the adduct formation between $Cu(DMG)_2$ and n-butylamine--especially in view of the fact that the infrared spectrum indicated that the basic structure of $Cu(DMG)_2$ was preserved in this product.

In Table 13 it can be seen that $Cu(DMG)_2$ is more soluble than the other two chelates in water, ethanol, and acetonitrile. These three solvents were shown to coordinate most strongly with $Cu(DMG)_2$ by the resolution of the visible spectra. Apparently, the interaction between each of these three solvents and $Cu(DMG)_2$ was great enough to overcome the difference in the enthalpies of solution in an inert solvent of $Cu(DMG)_2$ and $Ni(EMG)_2$.

In chloroform the order of increasing solubility was $Ni(EMG)_2 > Cu(DMG)_2 > Ni(DMG)_2$. Apparently, the interaction between chloroform and $Cu(DMG)_2$ is not nearly strong enough to compensate for the difference in the enthalpies of solution in an inert solvent of $Cu(DMG)_2$ and $Ni(EMG)_2$. In fact, the solubilities of $Cu(DMG)_2$ and $Ni(DMG)_2$ in chloroform indicate that the chloroform-$Cu(DMG)_2$ interaction just compensates for the difference in enthalpy of solution of these two chelates in an inert solvent. In the case of benzene, $Cu(DMG)_2$ is less soluble than either of the two nickel chelates. The interaction between $Cu(DMG)_2$ and benzene was was weakest in the series of solvents studied, and apparently was too weak to compensate even for the small difference in enthalpies of solution in an inert solvent of $Cu(DMG)_2$ and $Ni(EMG)_2$.

Some comment on the difference in the solubilities of $Ni(EMG)_2$ and $Ni(DMG)_2$ should be made at this point. For all the solvents listed in Table 12, $Ni(EMG)_2$ was significantly more soluble than $Ni(DMG)_2$; and the difference in solubility was greatest in chloroform and least in water. It does not seem logical to explain the higher solubility of $Ni(EMG)_2$ in the nonaqueous solvents listed as being due to the slightly greater organic character of the EMG radical-- especially in view of the fact that $Ni(EMG)_2$ was also slightly more soluble in water. A more logical explanation would seem to be some greater stabilizing force in the $Ni(DMG)_2$ crystal. This greater force could then be an interaction between adjacent nickel atoms in $Ni(DMG)_2$ (73, 77) which is not possible in $Ni(EMG)_2$.

4. Summary

$Cu(DMG)_2$ evidently tends to interact to some extent with all but the most inert solvents. On the other hand, $Ni(DMG)_2$ and $Ni(EMG)_2$ exhibit very little tendency to interact with solvent molecules. Thus the higher solubility of $Cu(DMG)_2$ relative to the solubilities of $Ni(EMG)_2$ and $Ni(DMG)_2$ in non-inert solvents is attributed to the greater ability of $Cu(DMG)_2$ to interact with the solvent and not to greater stability of the $Ni(EMG)_2$ and $Ni(DMG)_2$ crystals.

There does appear to be a difference in the stabilizing forces present in the crystals of $Ni(EMG)_2$ and $Ni(DMG)_2$. $Ni(EMG)_2$ was more soluble than $Ni(DMG)_2$ in all solvents studied. Because the solvents studied included water, in addition to organic solvents, the greater solubility of $Ni(EMG)_2$ could not be attributed to the greater organic character of this chelate. It therefore seemed logical to assume the presence of a greater stabilizing force in Ni(DMG)$_2$. A reasonable explanation for this greater stabilizing force is the weak Ni-Ni bond proposed by several groups of investigators (7, 8, 41, 73, 77).

The charge transfer spectra of Ni(DMG)$_2$, Ni(EMG)$_2$, and Cu(DMG)$_2$ are similar. Each contains several bands of high intensity. However, the energy of the charge transfer bands of Cu(DMG)$_2$ was sensitive to changes in solvent media; but the same was untrue for the charge transfer bands of Ni(DMG)$_2$ and Ni(EMG)$_2$. A mechanism was proposed to explain the variation of the charge transfer bands of Cu(DMG)$_2$ in different solvent media. In this mechanism the amount of dative character and normal covalent character in the Cu-N bond varies slightly from solvent to solvent. According to the proposed mechanism, the Ni-N bond would remain essentially dative in all solvents; and a variation in the charge transfer band with solvent would not be expected.

VII. SUMMARY

The nature of the difference in the solubility of $Cu(DMG)_2$ and $Ni(DMG)_2$ is apparently twofold. First of all there is a substantial rearrangement in the hydrogen bonding of $Cu(DMG)_2$ upon solution; whereas there is no significant difference between the hydrogen bonding of crystalline $Ni(EMG)_2$ and the hydrogen bonding of $Ni(EMG)_2$ in solution. What is true for $Ni(EMG)_2$ in solution would presumably be true for $Ni(DMG)_2$ in solution. Because $Cu(DMG)_2$ rearranges to form much stronger hydrogen bonds, the necessary energy is provided for $Cu(DMG)_2$ to sever its strong intermolecular bonds (Cu-O) and dissolve in inert solvents to about the same extent as $Ni(DMG)_2$.

The second difference in the nature of the solubility of $Cu(DMG)_2$ and $Ni(DMG)_2$ is the tendency of $Cu(DMG)_2$ to interact with all but the most inert solvents. On the other hand, $Ni(DMG)_2$ does not interact significantly with fairly polar solvents such as water or acetonitrile. In fact, $Ni(DMG)_2$ does not interact to an observable extent with good donor molecules such as _n_-butylamine. Thus it is the energy gained from solvent interaction that provides the necessary energy of solution to allow $Cu(DMG)_2$ to be more soluble than $Ni(DMG)_2$ in solvents such as ethanol, acetonitrile, and water.

It is interesting to note that if $Cu(DMG)_2$ did not undergo a hydrogen bond rearrangement upon solution and if $Cu(DMG)_2$ did not interact with all but the most inert solvents, then $Cu(DMG)_2$ should be significantly less soluble than $Ni(DMG)_2$ in all solvents. Thus $Cu(DMG)_2$ is nearly as soluble as $Ni(DMG)_2$ in inert solvents and more soluble in active solvents because of its unique characteristics and not because of any special stabilizing forces in crystalline $Ni(DMG)_2$.

VIII. SUGGESTIONS FOR FUTURE WORK

1) Whether each molecule of $Cu(DMG)_2$ interacts with one or two solvent molecules or with one or two donor molecules is still open to question. Dyrssen and co-workers (28, 29, 30) were able to measure the formation constant for the interaction of only one donor molecule with $Cu(DMG)_2$ utilizing solvent extraction and solubility data. However, Timerov, Yablokov, and Ablov (82) claimed that two solvent molecules occupied coordination sites around $Cu(DMG)_2$ in solution. The study of the visible spectra of $Cu(DMG)_2$ in different solvents could not resolve the problem because the distortion of a square planar copper(II) complex toward a tetragonal pyramid has the same effect on the d-orbital energy levels as the distortion toward an octahedral complex (25, 92). However, there is a possibility that this problem might be readily resolved by molecular weight determinations of $Cu(DMG)_2$ in various solvents. Molecular weights could also be determined for $Cu(DMG)_2$ solutions containing small concentrations of donor molecules or ions. The Thomas Isothermal Molecular Weight Apparatus, now available in this Laboratory, should be easily adaptable to these molecular weight determinations.

2) The interaction between Cu(DMG)$_2$ and hydroxide ion in aqueous solution could be studied more closely. By obtaining data similar to that presented in Fig. 24 on a pH meter which would read out the pH with an accuracy of 0.001 pH unit, one could determine the average number of hydroxide ions associated with each Cu(DMG)$_2$ molecule for several points in the titration. With this information the method of Bjerrum for the experimental measurement of stability constants (26, pp. 938-939) could be applied. With sufficiently accurate data one might be able to determine both the number of hydroxide ions interacting with each Cu(DMG)$_2$ molecule and also the stability constants for the interactions. The same technique could also be applied to the interaction of Cu(DMG)$_2$ with organic bases if a method could be found to measure the amount of free base.

3) It would be interesting to work out a method of analysis for small quantities of copper and nickel based on the behavior of the ultraviolet spectra of Cu(DMG)$_2$ and Ni(DMG)$_2$. When n-butylamine is added to a solution of Cu(DMG)$_2$, the molar absorptivity of the ultraviolet band occurring between 260 and 285 mμ increased. However, the intensity of the corresponding band in Ni(DMG)$_2$ was not

affected by the addition of n-butylamine. Thus, at a chosen wavelength the absorbance ($\underline{A}$) of a dilute mixture of Cu(DMG)$_2$ and Ni(DMG)$_2$ would be

$$\underline{A} = \underline{A}_{Ni} + \underline{A}_{Cu} = \epsilon_{Ni} c_{Ni} l + \epsilon_{Cu} c_{Cu} l, \qquad (1)$$

where $\underline{A}_{Ni}$ and $\underline{A}_{Cu}$ are the absorbances due to Ni(DMG)$_2$ and Cu(DMG)$_2$, respectively; ϵ_{Ni} and ϵ_{Cu} are the molar absorptivities of the respective chelates; c_{Ni} and c_{Cu} are the concentrations of Ni(DMG)$_2$ and Cu(DMG)$_2$; and l is the length of solution through which light passes. Now when n-butylamine is added to a similar quantity of the copper and nickel sample, $\underline{A}_{Ni}$ does not change, but $\underline{A}_{Cu}$ increases. The increase in the molar absorptivity of Cu(DMG)$_2$ as the concentration of n-butylamine is increased can be expressed as follows:

$$\epsilon'_{Cu} = \epsilon_{Cu} + f(b). \qquad (2)$$

Here f(b) represents some function of the concentration of n-butylamine.

Now the absorbance at a given wavelength would be

$$\underline{A} = \underline{A}_{Ni} + \underline{A}_{Cu} = \epsilon_{Ni} c_{Ni} l + \epsilon'_{Cu} c_{Cu} l. \qquad (3)$$

Therefore,

$$\underline{A} = \underline{A}_{Ni} + \underline{A}_{Cu} = \epsilon_{Ni}c_{Ni}l + \epsilon_{Cu}c_{Cu}l + f(b)c_{Cu}l \quad (4)$$

From equation 4 it can be seen that a plot of $\underline{A}$ versus the concentration of n-butylamine would yield a curve similar in shape to those in Fig. 17. If the point at which the curves level off is in some way indicative of the $Cu(DMG)_2$ concentration, then both nickel and copper could be determined because the intercept would give the combined concentrations of $Cu(DMG)_2$ and $Ni(DMG)_2$.

Such a scheme would certainly not be practical for the analysis of copper and nickel. Nevertheless, it would be interesting to see if it would work. The synergic effect which n-butylamine has on $Cu(DMG)_2$ is exhibited by other reagents for coordination compounds of other transition metals and of some lanthanide elements. Thus the principle of such an analysis has the remote possibility of being applicable to other situations where better methods of analysis are not available.

4) The OH and OD stretching frequencies should be determined for more compounds with O---O distances falling in the range of the abnormal isotope effect. For example,

$Pd(DMG)_2$ has an O---O distance of 2.49 A (74); and therefore, this compound should exhibit the abnormal isotope effect. Its infrared spectrum, along with the infrared spectrum of $Pd(DMG)_2$-d_2, should be re-examined with the knowledge of the abnormal isotope effect in mind. Such studies should add to the knowledge and understanding of the hydrogen bond and the metal-vic-dioximes.

5) The ultraviolet and visible spectra of crystalline $Cu(DMG)_2$, $Ni(DMG)_2$, and $Ni(EMG)_2$ were determined during the course of this research. The spectra, illustrated in Fig. 30, reveal a basic difference between the solid copper chelate and the two nickel chelates. This difference should be explained. The spectrum of crystalline $Cu(DMG)_2$ is practically the same as the ultraviolet and visible spectra of $Cu(DMG)_2$ in solution. However, in the case of the nickel chelates there is an intense band in the 500 mμ region which essentially disappears in the spectra of these nickel chelates in solution. It would be interesting to try to find an explanation for this spectral behavior that was compatible with the differences between the structure of crystalline $Cu(DMG)_2$ and the structures of the two nickel chelates. The intense band at the 500 mμ region for $Ni(DMG)_2$

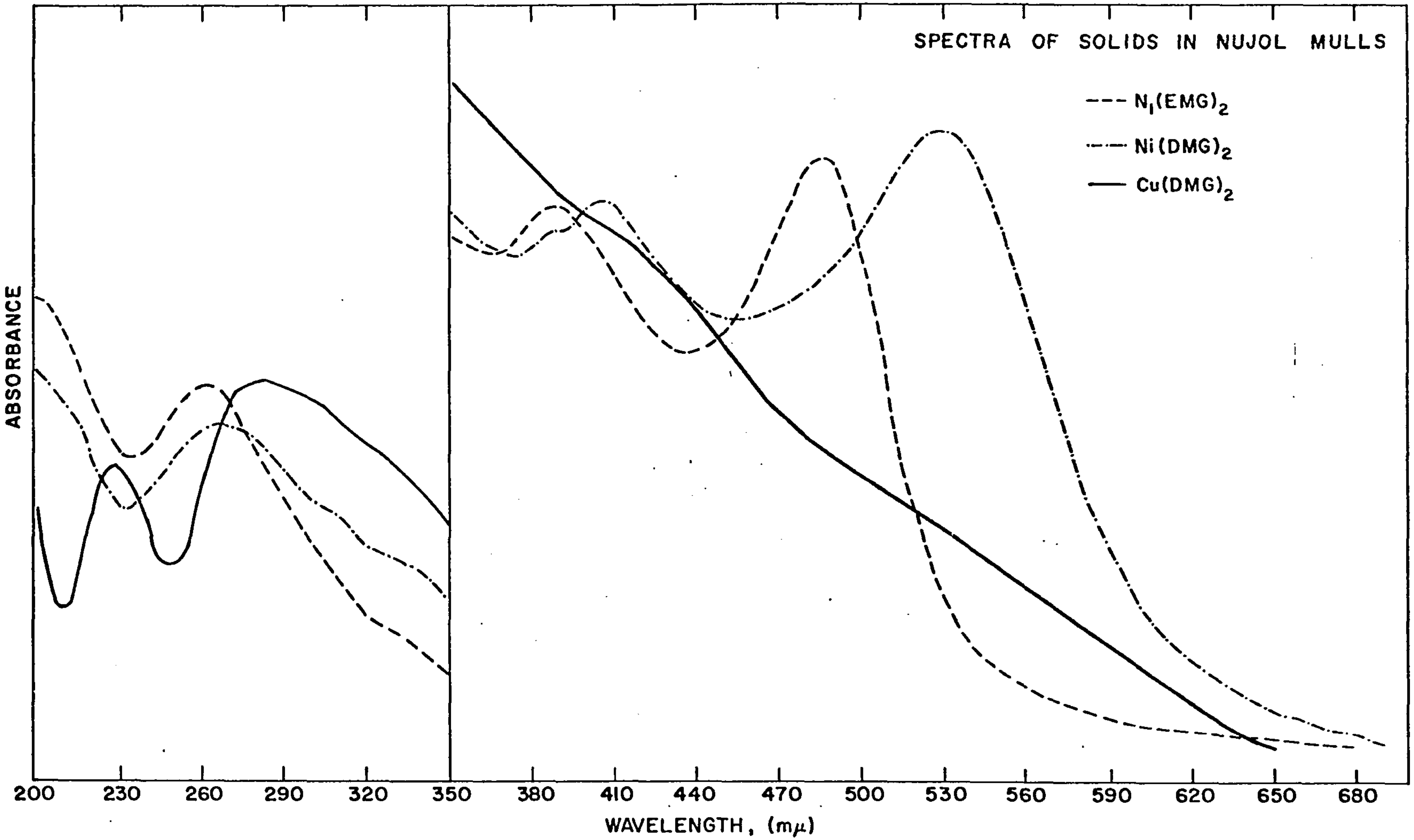


Fig. 30. Spectra of crystalline Ni(EMG)$_2$, Ni(DMG)$_2$, and Cu(DMG)$_2$

possibly arises due to the presence of the Ni-Ni bond in $Ni(DMG)_2$ (8); however, this could not be the case for $Ni(EMG)_2$ where Ni-Ni bonding is not possible. The spectra of these chelates in the crystalline state has been studied previously (8, 9).

6) The ODO distances should be determined for $Ni(DMG)_2$ and $Ni(EMG)_2$. Rundle (72) predicted that such short O---O distances as those in these nickel chelates should experience the normal isotope effect upon deuteration. However, this prediction has never been checked for distances shorter than the range where the abnormal isotope effect occurs.

7) The data obtained in this research indicate that the shorter OHO distance (2.53 A) in $Cu(DMG)_2$ exhibits the abnormal isotope effect. Therefore, the shorter ODO distance in $Cu(DMG)_2$-d_2 should be longer than 2.53 A. The ODO distances in $Cu(DMG)_2$-d_2 should be determined to see if the shorter O---O distance is really longer than 2.53 A.

IX. LITERATURE CITED

1. Anderson, S. Metal-metal bonds and physical properties of some nickel(II)-vic-dioxime complexes. Unpublished Ph.D. thesis. Ames, Iowa, Library, Iowa State University of Science and Technology. 1962.

2. Balz, G., Z. anorg. allgem. Chem., 231, 15 (1937).

3. Banks, C. V. vic-Dioximes as analytical reagents. In West, P. W., A. M. G. MacDonald, and T. S. West, eds. Analytical chemistry, 1962: proceedings Feigl Anniversary Symposium, Birmingham, England. pp. 131-144. Amsterdam, The Netherlands, Elsevier Publishing Company. 1963.

4. Banks, C. V., Record Chem. Progr., 25, 85 (1964).

5. Banks, C. V. and S. Anderson, J. Am. Chem. Soc. 84, 1486 (1962).

6. Banks, C. V. and S. Anderson, Inorg. Chem., 2, 112 (1963).

7. Banks, C. V. and D. W. Barnum, J. Am. Chem. Soc., 80, 3579 (1958).

8. Banks, C. V. and D. W. Barnum, J. Am. Chem. Soc., 80, 4767 (1958).

9. Basu, G., G. M. Cook, and R. L. Belfort, Inorg. Chem., 3, 1361 (1964).

10. Barker, M. F., Chem. News, 130, 99 (1925).

11. Beckman, E. and A. Köster, Ann., 274, 1 (1893).

12. Belfort, R. L., M. Calvin, and G. Belfort, J. Chem. Phys., 26, 1165 (1957).

13. Blinc, R. and D. Hadzi, J. Chem. Soc., 1958, 4536.

14. Blinc, R. and D. Hadzi, Mol. Phys., 1, 391 (1958).

15. Blinc, R. and D. Hadzi, Spectrochim. Acta, 16, 853 (1960).

16. Blinc, R. and D. Hadzi, and A. Novak, Z. Elektrochem., 64, 567 (1960).

17. Boardman, J. M. Lowest eigenfunction of a double-minimum potential well. Unpublished M.S. thesis. Ames, Iowa, Library, Iowa State University of Science and Technology. 1956.

18. Borello, E. and L. Henry, Compt. rend., 241, 1280 (1955).

19. Brady, O. L. and R. P. Mehta, J. Chem. Soc., 125, 2297 (1924).

20. Brady, O. L. and M. M. Muers, J. Chem. Soc. 1930, 1599.

21. Bryant, W. C. M. and C. M. Smith, J. Am. Chem. Soc., 57, 57 (1935).

22. Burger, K., I. Ruff, and F. Ruff, J. Inorg. Nucl. Chem., 27, 179 (1965).

23. Cambi, L. and L. Szegö, Ber., 64, 2591 (1931).

24. Charles, R. G. and H. Freiser, Anal. Chim. Acta, 11, 101 (1954).

25. Companion, A. L. and M. A. Komarynsky, J. Chem. Educ., 41, 257 (1964).

26. Cotton, F. A. and G. Wilkinson. Advanced inorganic chemistry. New York, New York, Interscience Publishers. 1962.

27. Cox, E. G., E. Sharratt, W. Wardlaw, and K. C. Webster, J. Chem. Soc., 1936, 129.

28. Dyrssen, D., Svensk. Kem. Tidskr., 75, 618 (1963).

29. Dyrssen, D. and M. Hennichs, Acta Chem. Scand., 15, 47 (1961).

30. Dyrssen, D. and D. Petkovic, Acta Chem. Scand., 19, 653 (1965).

31. Feilchenfeld, H., J. Phys. Chem., 62, 117 (1958).

32. Ferrano, J. R., J. Chem. Educ., 38, 201 (1961).

33. Fleischer, D. A thermodynamic study of some factors affecting the stability and solubility of metal chelates. Microfilm Copy No. 59-2396, unpublished Ph.D. thesis, University of Pittsburgh, Pittsburgh, Pennsylvania. Ann Arbor, Michigan, University Microfilms, Inc. 1959.

34. Frasson, E., R. Bardi, and S. Bezzi, Acta Cryst., 12, 201 (1959).

35. Frasson, E. and C. Panattoni, Acta Cryst., 13, 893 (1960).

36. Frasson, E., C. Panattoni, and R. Zannetti, Acta Cryst., 12, 1027 (1959).

37. Fritz, J. S., J. E. Abbink, and M. A. Payne, Anal. Chem., 33, 1381 (1961).

38. Fritz, J. S. and G. S. Hammond. Quantitative organic analysis. New York, New York, John Wiley and Sons, Inc. 1957.

39. Fujita, J., A. Nakahara, and R. Tsuchida, J. Chem. Phys., 20, 1487 (1952).

40. Ginn, S. G. W. and J. L. Wood, Proc. Chem. Soc., 1964, 370.

41. Godycki, L. E. and R. E. Rundle, Acta Cryst., 6, 487 (1953).

42. Godycki, L. E., R. E. Rundle, R. C. Voter, and C. V. Banks, J. Chem. Phys., 19, 1205 (1951).

43. Hadzi, D., *J. Chem. Phys.*, *34*, 1445 (1961).

44. Hantzsch, A., *Ber.*, *24*, 13 (1891).

45. Hantzsch, A. and A. Werner, *Ber.*, *23*, 11 (1890).

46. Hooker, D. T. Preparation, properties, and analytical applications of some substituted alicyclic *vic*-dioximes. Unpublished Ph.D. thesis. Ames, Iowa, Library, Iowa State University of Science and Technology. 1955.

47. Jones, L. H., R. M. Badger, and G. E. Moore, *J. Chem. Phys.*, *19*, 1599 (1951).

48. Jorgensen, C. K. Absorption spectra and chemical bonding in complexes. Reading, Massachusetts, Addison-Wesley Publishing Company, Inc. 1962.

49. Klemm, W., H. Jacobi, and W. Tilk, *Z. anorg. allgem. Chem.*, *201*, 1 (1931).

50. Kolthoff, I. M. and E. B. Sandell. Textbook of quantitative inorganic analysis. 3rd ed. New York, New York, The Macmillan Company. 1952.

51. Krause, R. A., D. C. Jicha, and D. H. Busch, *J. Am. Chem. Soc.*, *83*, 528 (1961).

52. Lippincott, E. R. and R. Schroeder, *J. Chem. Phys.*, *23*, 1099 (1955).

53. Lord, R. C. and R E. Merrifield, *J. Chem. Phys.*, *21*, 166 (1953).

54. McWhinnie, W. R., *J. Inorg. Nucl. Chem.*, *27*, 1063 (1965).

55. Meisenheimer, J., *Ber.*, *54*, 3206 (1921).

56. Milone, M. and E. Borello, *Gazz. Chim. Ital.*, *85*, 500 (1955).

57. Mulliken, R. S., *J. Am. Chem. Soc.*, *74*, 811 (1952).

58. Nakagawa, I., R. J. Hooper, J. L. Walter C. S. C., and T. J. Lane C. S. C., Spectrochim. Acta, 21, 1 (1965).

59. Nakahara, A., Bull. Chem. Soc. Japan, 28, 473 (1955).

60. Nakahara, H., J. Fujita, and R. Tsuchida, Bull. Chem. Soc. Japan, 29, 296 (1956).

61. Nakamoto, K., M. Margoshes, and R. E. Rundle, J. Am. Chem. Soc., 77, 6480 (1955).

62. Panattoni, C., E. Frasson, and R. Zannetti, Gazz. Chim. Ital., 89, 2132 (1959).

63. Pauling, L., J. Am. Chem. Soc., 53, 1367 (1931).

64. Pfeiffer, P., Ber., 63, 1811 (1930).

65. Pfeiffer, P. and J. Richarz, Ber., 61, 103 (1928).

66. Pimentel, G. C. and C. H. Sederholm, J. Chem. Phys., 24, 639 (1956).

67. Ray, P. and D. N. Sen, J. Indian Chem. Soc., 25, 473 (1948).

68. Reid, C. and R. S. Mulliken, J. Am. Chem. Soc., 76, 3869 (1954).

69. Roos, B., Acta Chem. Scand., 18, 2186 (1964).

70. Rundle, R. E., J. Am. Chem. Soc., 76, 3101 (1954).

71. Rundle, R. E., J. Chem. Phys., 21, 937 (1953).

72. Rundle, R. E., J. Phys. (Paris), 25, 487 (1964).

73. Rundle, R. E. and C. V. Banks, J. Phys. Chem., 67, 508 (1963).

74. Rundle, R. E. and M. Parasol, J. Chem. Phys., 20, 1487 (1952).

75. Sabatini, A., L. Sacconi, and V. Schettino, Inorg. Chem., 3, 1775 (1964).

76. Sacconi, L., A. Sabatini, and P. Gans, Inorg. Chem., 3, 1772 (1964).

77. Sharpe, A. G. and D. B. Wakefield, J. Chem. Soc., 1957, 281.

78. Shimanouchi, T. and I. Nakagawa, Inorg. Chem., 3, 1805 (1964).

79. Snyder, R. G. and J. A. Ibers, J. Chem. Phys., 36, 1356 (1962).

80. Thilo, E. Sammlung chemischer und chemisch-technischer Vortrage. Neue Folge Heft 13. Stuttgart, Germany, Ferdinand Enke. 1932.

81. Thilo, E. and H. Friedrich, Ber., 62, 2990 (1929).

82. Timerov, R. Kh., Yu. V. Yablokov, and A. V. Ablov, Proc. Acad. Sci. USSR, Phys. Chem. Sect. English Transl., 152, 786 (1963).

83. Tschugaeff, L., J. Chem. Soc., 105, 2187 (1914).

84. Tschugaeff, L., Z. anorg. Chem., 46, 144 (1905).

85. Ungande, H. E., G. Fritz, and L. W. Kissinger, Tetrahedron, 19, 235 (1963).

86. Voter, R. C. Inner-complex compounds of alicylic vic-dioximes. Unpublished Ph.D. thesis. Ames, Iowa, Library, Iowa State University of Science and Technology. 1951.

87. Voter, R. C., C. V. Banks, V. A. Fassel, and P. W. Kehres, Anal. Chem., 23, 1730 (1951).

88. Werner, A. and P. Pfeiffer. Neuere Anschauungen im Gebeit der Anorganischen Chemie. Braunschweig, Germany, Friedrich Vieweg und Sohn. 1905.

89. Wiersema, A. K. and J. J. Windle, *J. Phys. Chem.*, *68*, 2316 (1964).

90. Williams, D. E., G. Wohlauer, and R. E. Rundle, *J. Am. Chem. Soc.*, *81*, 755 (1959).

91. Yamada, S. and R. Tsuchida, *J. Am. Chem. Soc.*, *75*, 6351 (1953).

92. Zuckerman, J. J., *J. Chem. Educ.*, *42*, 315 (1965).

X. ACKNOWLEDGMENTS

I wish to express my gratitude to Professor Charles V. Banks for the suggestions and helpful discussions offered throughout the course of this research. His interest and his encouragement were greatly appreciated.

To Miss Evelyn Conrad I wish to express my sincere thanks for obtaining the infrared spectra. Miss Conrad is quite accomplished at achieving well resolved spectra of difficult samples. She also offered helpful suggestions concerning the interpretation of the spectra.

Finally, I am indebted to my wife, who, while working on her own research, gave the moral support and encouragement which made this work possible.