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Solubility behavior of the nickel(II)-, palladium(II)-, and platinum(II)- complexes of some vic-dioximes

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SOLUBILITY BEHAVIOR OF THE NICKEL(II)-, PALLADIUM(II)-,
AND PLATINUM(II)- COMPLEXES OF SOME VIC-DIOXIMES

by

David Warren Smith

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

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Iowa State University
Ames, Iowa

1968

TABLE OF CONTENTS

	Page
I. INTRODUCTION	1
II. LITERATURE REVIEW	7
III. REAGENTS	27
IV. EXPERIMENTAL	30
V. DISCUSSION AND CONCLUSIONS	66
VI. SUMMARY	75
VII. SUGGESTIONS FOR FUTURE WORK	77
VIII. BIBLIOGRAPHY	79
IX. ACKNOWLEDGMENTS	85

I. INTRODUCTION

A. Purpose of Research

The discovery of the reaction of nickel(II) with dimethylglyoxime by the Russian chemist Tschugaeff (78) in 1905 has led to an extensive study of the chemistry of the metal-vic-dioxime chelates. Numerous studies of the coordination chemistry of the metal-vic-dioximes have been made to explain their unique properties. Such investigations have included the determination of crystal structures, spectral and magnetic studies, and application of the law of mass action to equilibrium studies of chemical reactions in solution.

The vic-dioximes are well-known as selective gravimetric reagents for the determination of nickel and palladium. It has been suggested that the selectivity of the vic-dioximes for these metals is due to the ability of their chelates to pack in their respective crystals in such a way that chains of weak intermolecular metal-metal bonds are formed (47). The metal-metal bonds formed in this type of packing are said to contribute enough stability to the crystal that it is insoluble in water, and the unique packing tends to prevent coprecipitation of other metals (9). Several studies have been interpreted as support for this hypothesis (7,8,9,10,88,76).

Recently, other investigators (60,90,14,4) have reexamined the solution and solid state spectral properties of these chelates and have questioned the hypothesis of metal-metal

bonding in the metal-vic-dioxime crystals.

The purpose of this research is to investigate some properties of a series of vic-dioxime chelates of nickel(II), palladium(II), and platinum(II) which have crystal structures with chains of metal atoms along the long axis of the needle-like crystals where metal-metal bonding of the type proposed could possibly occur. Nickel ethylmethylglyoxime, which has a crystal structure (43) in which no chain of nickel atoms forms and no metal-metal bonding is possible, was used for comparison purposes. This investigation should provide a test for the metal-metal bonding hypothesis and more information for constructing a model to explain the properties of the metal-vic-dioximes.

Values of the thermodynamic constants relating to the dissolution process of the metal-vic-dioximes in n-heptane and carbon tetrachloride were determined. The heats of solution of the chelates in these solvents have been taken as a measure of their relative crystal energies (7,73,40). The heats of solution have been evaluated considering the crystalline structural features of the metal-vic-dioximes to determine what factors are important in stabilizing the crystals.

Thermal and spectral studies were made to determine if any other factors, such as solid state effects or solvation effects, are important in the solubility behavior of the series of compounds considered.

It is hoped that the results of this work will add to the understanding of the chemistry of the metal-vic-dioximes and further the development of improved analytical procedures and reagents.

B. Nomenclature and Notation

In this thesis the vic-dioximes and their chelates will, in general, be called by their trivial names or noted by abbreviation. The structures, systematic names, trivial names, and abbreviations of some representative compounds used in this work are listed in Table 1. Any compounds not listed will be similar enough to those in the table that their structure will be apparent.

The systematic names of the vic-dioximes are those proposed by the International Union of Chemistry (67). The systematic naming of complex compounds is based on the general rules set forth by Fernelius et al. (38).

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

Table 2 defines some special terms and abbreviations which have been adopted for this manuscript. Any other abbreviations

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

Structure	Systematic name trivial name abbreviation
$ \begin{array}{c} \text{OH} \\ \\ \text{N} \\ \\ \text{CH}_3 - \text{C} - \text{C} - \text{CH}_3 \\ \\ \text{N} \\ \\ \text{HO} \end{array} $	syn-2,3-butanedionedioxime syn-dimethylglyoxime syn-DMG
$ \begin{array}{c} \text{OH} \quad \text{OH} \\ / \quad \backslash \\ \text{N} \quad \text{N} \\ \quad \\ \text{CH}_3 - \text{C} - \text{C} - \text{CH}_3 \end{array} $	amphi-2,3-butanedionedioxime amphi-dimethylglyoxime amphi-DMG
$ \begin{array}{c} \text{OH} \\ \\ \text{N} \\ \\ \text{CH}_3 - \text{C} - \text{C} - \text{CH}_3 \\ \\ \text{N} \\ / \\ \text{HO} \end{array} $	anti-2,3-butanedionedioxime anti-dimethylglyoxime anti-DMG
$ \begin{array}{c} \text{OH} \\ \\ \text{N} \\ \\ \text{CH}_3 - \text{C} - \text{C} - \text{CH}_2\text{CH}_3 \\ \\ \text{N} \\ / \\ \text{HO} \end{array} $	2,3-pentanedionedioxime ethylmethylglyoxime EMG

Table 1. (Continued)

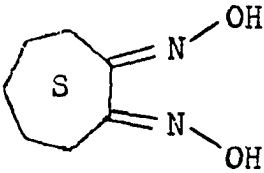
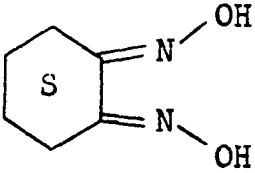
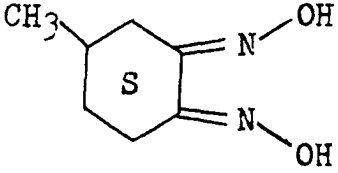
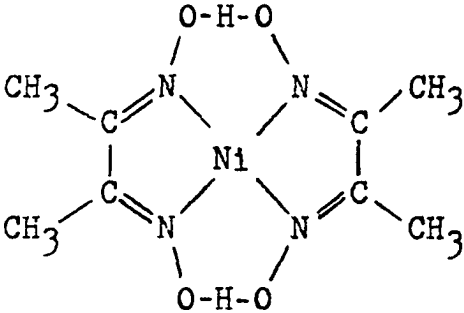
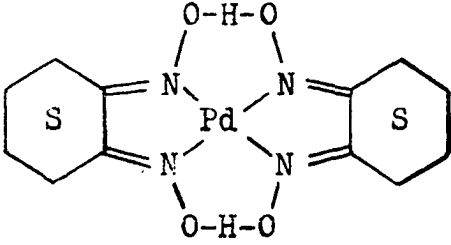
Structure	Systematic name trivial name abbreviation
	1,2-cycloheptanedione dioxime heptoxime Heptox
	1,2-cyclohexanedione dioxime nioxime Niox
	4-methyl-1,2-cyclohexane- dione dioxime 4-methylnioxime 4-MeNiox
	bis(2,3-butanedione dioximate- <u>N,N'</u>)nickel(II) nickel dimethylglyoxime Ni(DMG) ₂
	bis(1,2-cyclohexanedione- dioximate- <u>N,N'</u>)palladium(II) palladium nioxime Pd(Niox) ₂

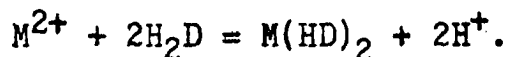
Table 2. Special terms and abbreviations adopted for manuscript

Term or abbreviation	Definition
H ₂ D	acid form of a <u>vic</u> -dioxime
HD ⁻	basic form of a <u>vic</u> -dioxime
M	a metal atom
color band	lowest energy, solid state, visible absorption band of the metal- <u>vic</u> -dioximes which gives rise to their characteristic colors
α-Benzil	α-benzildioxime
α-Furil	α-furildioxime
4-IsopNiox	4-isopropylnoxime
POPO	2,5-diphenyloxazole
POPOP	p-bis[2-(5-phenyloxazolyl)]-benzene
EDTA	ethylenediaminetetraacetic acid
X ₂	mole fraction of solute
K _{s2}	[M(HD) ₂], intrinsic solubility constant (solution saturated with M(HD) ₂)
pK _{s2}	-log K _{s2}
β ₂	[M(HD) ₂][M ²⁺] ⁻¹ [HD ⁻] ⁻²
χ _M	molar magnetic susceptibility

viations used in this manuscript will be defined in the text or will be the standard abbreviations of common terms which will conform to the recommendations of the American Chemical Society (2).

II. LITERATURE REVIEW

Tschugaeff (78) first reported the reactions of vic-dioximes with nickel(II), palladium(II), platinum(II), and copper(II) according to the equation¹



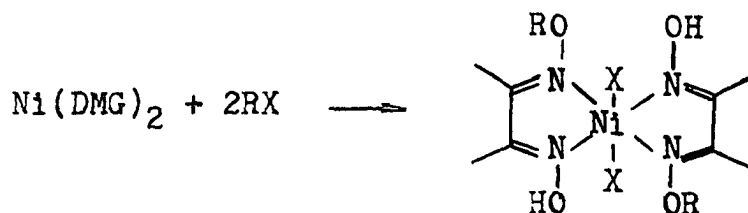
He noted that the nickel, palladium, and platinum compounds sublime in a vacuum and are non-electrolytes and that they are insoluble in water and common organic solvents. He also stated that $Cu(DMG)_2$ does not sublime and is soluble in water.

In 1921 Meisenheimer (59) showed that of the three stereoisomers of a vic-dioxime, designated syn, amphi, and anti, as drawn in Table 1, it is the anti isomer that is responsible for the formation of the 2:1 chelate.

Brady and Muers (22) proposed a structure for $Ni(DMG)_2$ based entirely on chemical evidence which closely resembled the structure later determined by x-ray technique. They indicated a preference for a hydrogen bonded structure since this would account for the unreactive nature of the hydroxyl groups which they and other workers (79,13) observed. The unreactivity of the hydroxyl groups in metal-vic-dioximes is quite remarkable (53), but the -OH group will react with some rather harsh reagents. Busch and his coworkers (26,55) have clari-

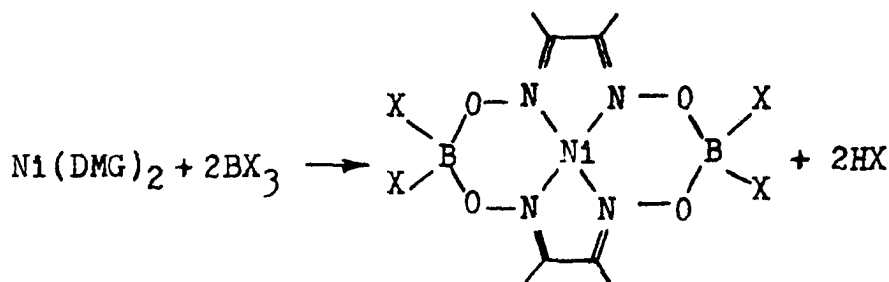
¹See the INTRODUCTION for an explanation of symbols and nomenclature.

fied the conflicting reports on the reactions of the coordinated vic-dioximes. They have confirmed that $\text{Ni}(\text{DMG})_2$ reacts with methyl iodide and dimethylsulfate according to the equation



and that $\text{Ni}(\text{DMG})_2$ reacts with acetylchloride in a rather complex manner.

Schrauzer (74) has reported the reaction of the $\text{Ni}(\text{DMG})_2$ with boron compounds of the type BX_3 , where $\text{X} = \text{F}, \text{CH}_3, \underline{n}\text{-C}_3\text{H}_7\text{-}, \underline{n}\text{-C}_4\text{H}_9\text{-},$ and isobutyl. The reaction is formulated to be



The vic-dioxime chelates of nickel and palladium have been shown to be diamagnetic by several workers (27,54,12). Willis and Mellor (86) have shown that the magnetic moment of nickel methylglyoxime rises to 1.5 BM in pyridine solution, which indicates an increase in the coordination number of nickel.

The accurate determination of the structure of nickel dimethylglyoxime by Godycki and Rundle (47) was an important step in the understanding of the metal-vic-dioximes. The

structure data were later refined by Williams, Wohlaer, and Rundle (85). The $\text{Ni}(\text{DMG})_2$ molecule was found to be nearly square planar and to have the bond lengths and angles as shown in Figure 1. Nickel positions in the crystal are 000 , $00\frac{1}{2}$, $\frac{1}{2}\frac{1}{2}\frac{1}{2}$, and $\frac{1}{2}\frac{1}{2}0$. The nickel atoms lie in a straight row that extends along the long axis of the needle-like crystal, as shown in Figure 2. The distance between two adjacent nickel atoms was found to be $3.245\overset{\circ}{\text{A}}$. After considering the length of the intermolecular nickel-nickel distance, the unusual dichroism of the crystals, and the solubility difference between $\text{Ni}(\text{DMG})_2$ and $\text{Cu}(\text{DMG})_2$, Godycki and Rundle suggested that weak metal-metal bonds are formed in the crystalline state of $\text{Ni}(\text{DMG})_2$. Besides the unique packing in the crystals, the very short intramolecular hydrogen bond is another striking structural feature of $\text{Ni}(\text{DMG})_2$.

$\text{Pd}(\text{DMG})_2$ (66) and $\text{Pt}(\text{DMG})_2$ (44) have been shown to be isomorphous with $\text{Ni}(\text{DMG})_2$.

The molecular structure of nickel ethylmethylglyoxime was found by Frasson and Panattoni (43) to be quite similar to that of nickel dimethylglyoxime. However, the molecules of $\text{Ni}(\text{EMG})_2$ are packed into the crystal in a manner such that the nickel atoms do not form long chains as in $\text{Ni}(\text{DMG})_2$. Table 3 lists structural data for the compounds considered in this study.

As previously mentioned, the selectivity of the vic-

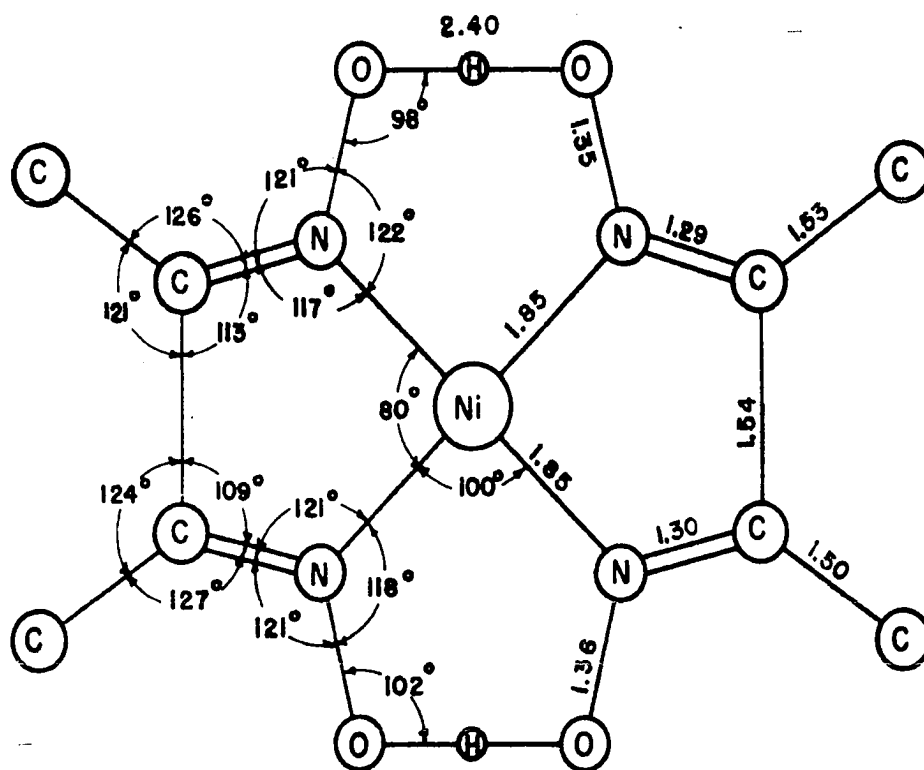


Figure 1. Bond lengths and bond angles in Ni(DMG)₂

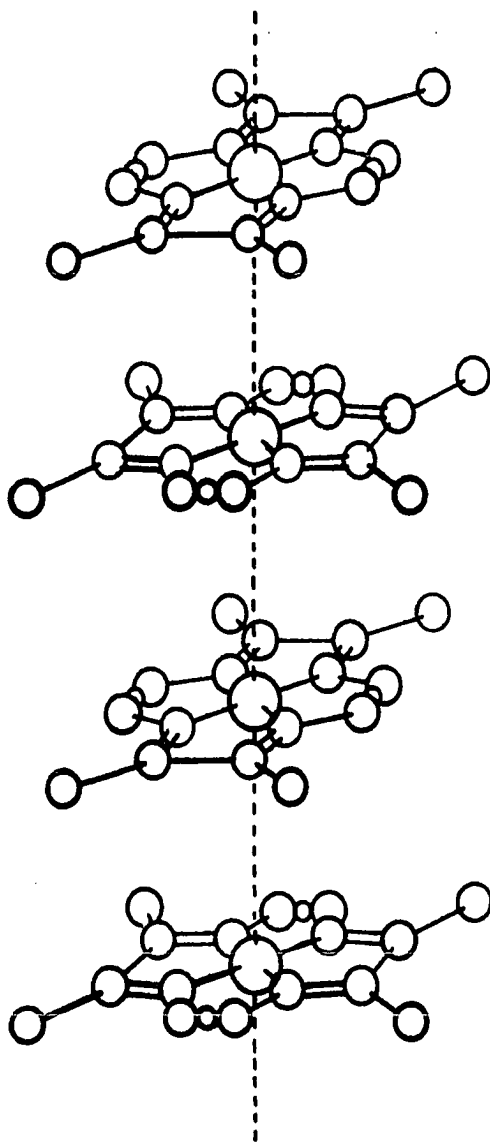


Figure 2. Crystal structure of $\text{Ni}(\text{DMG})_2$

Table 3. Structural data and position of the solid state color band in some vic-dioxime chelates of nickel, palladium, and platinum

Chelate	Interatomic distance, (Å)				Bond angle, (degrees)		Color band $\lambda_{\text{max.}}$ (m μ) ^b	Structure reference
	M-M	O-O	M-N ^a	N-O ^a	N-M-N	M-N-O		
Ni(4-IsopNiox) ₂	3.19						557	9
Ni(DMG) ₂	3.233	2.40	1.85	1.355	80	120	554	47,85
Ni(Niox) ₂	3.237						552	9
Ni(4-MeNiox) ₂	3.24						547	9
Ni(3-MeNiox) ₂	3.47						503	9
Ni(Heptox) ₂	3.596						465	9
Ni(EMG) ₂	4.75 3.44 ^d	2.33	1.855	1.38	82	121	506 ^c	43
Pd(DMG) ₂	3.255	2.62	1.935	1.34	81	122.5	480	66
Pt(DMG) ₂	3.235	3.03	1.94	1.275	83	134.5	625 ^e	44

^aMean values.

^bTaken from Banks and Barnum (10).

^cColloidal spectrum, taken from Anderson (3).

^dM-O distance.

^eSodium chloride pellet transmission spectrum, taken from Basu et al. (14).

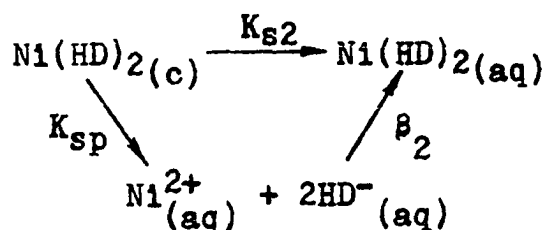
dioximes has been attributed to the metal-metal bonding in their chelates of nickel, palladium, and platinum. With this view in mind, Hooker (51) prepared a series of substituted alicyclic vic-dioximes and found the nickel and palladium chelates to be many times more soluble in chloroform than the corresponding nioxime chelates. The bulkiness of the ligand was taken as a rough measure of the metal-metal distances in the chelates.

Banks and Barnum (9) measured the metal-metal distance in the crystals of a series of metal-vic-dioximes by x-ray techniques. Several of these chelates were found to be isostructural to $\text{Ni}(\text{DMG})_2$ (47,9). Table 3 lists structural data for some of the compounds they considered. Banks and Barnum were able to establish only a rough correlation between the metal-metal distance and the solubility product constant for several of the chelates.

In another study Banks and Barnum (10) observed that colloidal suspensions of the nickel-vic-dioximes give an absorption band in the visible region of the spectrum which is not found in the spectra of the chelates when dissolved in chloroform and 1,2-dichlorobenzene. This absorption band is responsible for the characteristic colors of the solid metal vic-dioximes considered in this study and will be henceforth called the color band. Banks and Barnum suggested that the color band was due to metal-metal bond formation in the solid

state. However, it was later observed that $\text{Ni}(\text{EMG})_2$, for which metal-metal bonding is not considered possible, also exhibits the color band in colloidal suspensions (3). The positions of the solid state color band for some of the metal-vic-dioximes as measured by Banks and Barnum are given in Table 3.

In attempting to explain the solubility behavior of the metal-vic-dioximes, many researchers have determined their solubilities in various solvents and the thermodynamics of dissolution. Banks and Anderson (8) determined the intrinsic solubility constant, K_{s2} , and found that it correlated better with the metal-metal distance than did the solubility product constant. This was not unexpected, they noted, because the intrinsic solubility is more closely related with the crystal energy than is the solubility product and might be less subject to ligand effects.



$\text{Ni}(\text{DMG})_2$ was found not to fit on the curve correlating $\text{p}K_{s2}$ and nickel-nickel distance for an alicyclic series of vic-dioxime chelates. Banks suggested that other factors than nickel-nickel distance may be important and that the intrinsic solubilities of the series in a non-coordinating solvent

might very well be expected to correlate better with nickel-nickel bond distance than is observed in water (6).

Banks and Anderson (7) also determined the heats of solution for $\text{Ni}(\text{DMG})_2$ and $\text{Ni}(\text{EMG})_2$ in a number of solvents. They found that in non-coordinating solvents such as carbon tetrachloride and n-heptane the heat of solution of the nickel dimethylglyoxime is about 10 kcal greater than that of nickel ethylmethylglyoxime and suggested that this probably is a fairly good measure of the nickel-nickel bond strength. It is interesting to note that Rundle (71) had earlier predicted such a bond strength for $\text{Ni}(\text{DMG})_2$ from solubility considerations of $\text{Ni}(\text{DMG})_2$ and $\text{Cu}(\text{DMG})_2$.

Dyrssen (35) has pointed out, however, that it might be unreliable to base a discussion of the different bond energies in the solid state on the solubilities of the metal-vic-dioximes in inert solvents, such as n-heptane. He suggests that possible rearrangements of the hydrogen bond system of the chelates upon dissolution could make a dominating contribution to the solubility.

Wood and Jones (87) have determined the heats of sublimation for nickel glyoxime and nickel dimethylglyoxime to be 13.4 and 7.7 kcal/mole, respectively. They used an isoteniscope technique to measure the vapor pressures over a range of temperatures. However, Wood and Jones noted some decomposition in some of the compounds they studied by this method.

Several infrared spectral investigations of the metal-vic-dioximes have been made. These studies have been mainly concerned with the strong intramolecular hydrogen bonds known to be present in these compounds. However, there has been little agreement about the location of the OH stretching vibration. Some investigators (45,62,63,70,82) have indicated that they believed the OH stretching vibration to occur in the 1700 cm^{-1} region, but Blinc and Hadzi have maintained the OH stretching vibration occurs in the 2300 cm^{-1} region (18,19, 20). While the 2300 cm^{-1} band is quite weak in all spectra reported, the assignments of Blinc and Hadzi demanded favorable attention because they reported two OH stretching vibrations for crystalline $\text{Cu}(\text{DMG})_2$.

Later, it was revealed by x-ray determination of the crystal structure of $\text{Cu}(\text{DMG})_2$ that it exists as a dimer in the crystal joined by two Cu-O bonds (42). Consequently, there are two different O---O distances, one of $2.53\overset{\circ}{\text{A}}$ and the other of $2.70\overset{\circ}{\text{A}}$. These two different O---O distances would be expected to give rise to two OH stretching bands.

Blinc and Hadzi have also claimed that $\text{Cu}(\text{DMG})_2$ and $\text{Ni}(\text{DMG})_2$ 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 (49) has explained the presence of two bands in a hydrogen bonded compound as being due to the splitting of the vibrational energy levels due to proton

tunnelling. Hadzi also 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. Of the five hydrogen bonded compounds (the metal-vic-dioximes not included) which Hadzi studied, he found bands between 100 and 160 cm^{-1} . The bands disappeared upon deuteration; Hadzi believed they shifted to frequencies below 100 cm^{-1} .

Caton (28) studied the solid state (crystalline) and solution infrared spectra of $\text{Cu}(\text{DMG})_2$, $\text{Ni}(\text{DMG})_2$, and $\text{Ni}(\text{EMG})_2$. He found that improved mull spectra of the crystalline chelates in the 2000 cm^{-1} to 2800 cm^{-1} region could be obtained by extra grinding. Table 4 gives the assignments of the OH and OD bands made by Caton.

Table 4. Frequency of OH and OD bands of $\text{Cu}(\text{DMG})_2$, $\text{Ni}(\text{EMG})_2$, and $\text{Ni}(\text{DMG})_2$

Chelate	State ^a	R ^b	$\nu_{\text{OH}}^{\text{c}}$	$\nu_{\text{OD}}^{\text{c}}$	$\delta_{\text{OH}}^{\text{d}}$	$\delta_{\text{OD}}^{\text{d}}$
$\text{Cu}(\text{DMG})_2$	C	2.70	2650	1977	1492	1175
	C	2.53	2382	2370	1640	1262
	S	----	2375	1675	1640	1274
$\text{Ni}(\text{EMG})_2$	C	2.33	2388	1515	1784	1209
	S	----	2350	1512	1715	1253
$\text{Ni}(\text{DMG})_2$	C	2.40	2322	1530	1790	1275

^aC is solid or crystalline state; S indicates in solution.

^bR is OHO distance in \AA .

^c ν is stretching frequency in cm^{-1} .

^d δ is bending frequency in cm^{-1} .

Caton reached the following conclusions from his work:

1. $\text{Ni}(\text{DMG})_2$ has a band at 2322 cm^{-1} which disappears upon deuteration of the hydrogen bond system with a new band appearing at 1530 cm^{-1} . He assigned this band as the OH stretching vibration.
2. The more strongly hydrogen bonded OHO group in $\text{Cu}(\text{DMG})_2$ (O---O distance = $2.53\overset{\circ}{\text{A}}$) has approximately the same OH stretching frequency as the OHO groups in $\text{Ni}(\text{DMG})_2$ and $\text{Ni}(\text{EMG})_2$ which have significantly shorter O---O distances in the crystalline state. This can be interpreted using the model of Lippincott and Schroeder (57) which predicts that the increase in OH frequency shift as the O---O distance decreases should have a maximum. This maximum, which Lippincott and Schroeder calculated to occur at an O---O distance of $2.45\overset{\circ}{\text{A}}$, corresponds to the case of symmetrical hydrogen bonding. The O---O distance of $2.53\overset{\circ}{\text{A}}$ for $\text{Cu}(\text{DMG})_2$ falls on one side of the maximum; whereas the shorter O---O distances of the nickel chelates occur at a corresponding point on the opposite side; thus explaining how one OH stretching frequency could be found for two different O---O distances.
3. Upon solution of $\text{Cu}(\text{DMG})_2$ only one OH stretching band remains at 2375 cm^{-1} . This result supports

the prediction of Rundle and Banks (73) that the solubility difference between $\text{Ni}(\text{DMG})_2$ and $\text{Cu}(\text{DMG})_2$ is due in large part to a gain in energy resulting from the rearrangement of the hydrogen bond system in $\text{Cu}(\text{DMG})_2$ and the interaction of the dissolved monomers of $\text{Cu}(\text{DMG})_2$ with the solvent rather than a difference in their crystal energies (29).

4. There is little difference between the spectra of the chelates in their hydrogen form and the deuterium-substituted chelates in the 500 to 100 cm^{-1} range. If the lowest vibrational energy-level of the OH bond had been split due to proton tunnelling in an asymmetrical OHO bond, one might have expected a band in this region to have disappeared on deuteration (49). Therefore, the behavior of the far infrared spectrum is consistent with the presence of symmetrical OHO bonds; however, the far infrared spectra alone do not constitute any evidence for symmetrical OHO bonds.

Chu and Barrow (31) have reported the matrix isolated infrared spectra of $\text{Ni}(\text{DMG})_2$ and $\text{Pd}(\text{DMG})_2$ in KBr. Vapor streams of KBr and chelate were produced in a vacuum by heating two quartz crucibles, one containing the KBr and the other containing the chelate. The partially collimated vapor streams were deposited simultaneously on the Pyrex surface of a

liquid-nitrogen well. The deposit was then scraped off the Pyrex surface and pressed into a pellet. The resulting spectra differed from that of KBr pellets formed in the usual manner. Chu and Barrow noted that the KBr pellet of the matrix-isolated $\text{Ni}(\text{DMG})_2$ appeared yellow rather than red as in the KBr pellet prepared in the usual manner. The yellow pellets were noted to change to red when heated for 15 minutes at 160° or by passing pyridine through them. This indicated that they probably had achieved complete isolation of the chelate molecules and that the entrapped molecules are quite mobile. No assignments of the infrared spectral bands were made by these workers.

Recently, Drugov (34) has made an infrared spectral study of some vic-dioxime chelates of nickel(II). He calculated the O---O bond length for $\text{Ni}(\text{DMG})_2$, $\text{Ni}(\alpha\text{-Benzil})_2$, $\text{Ni}(\text{Niox})_2$, $\text{Ni}(\text{Heptox})_2$, and $\text{Ni}(\alpha\text{-Furil})_2$ as 2.44, 2.42, 2.43, 2.43, and 2.45⁰_Å, respectively. These calculations were based on the Nakamoto et al. relationship (64) which has been shown to be invalid for very short hydrogen bond systems (57,28).

The unique optical properties of the metal-vic-dioximes have long been an object of considerable study and controversy.

Tschugaeff (78) first reported that some of the metal-vic-dioximes are dichroic. If the needle-like crystals of $\text{Ni}(\text{DMG})_2$ are observed with plane polarized light, they are red when the electric vector of the polarized light is

parallel to the needle axis of the crystal (perpendicular to the molecular planes), but orange when the electric vector of the polarized light is perpendicular to the needle axis.

As noted earlier, the unusual dichroism of crystalline $\text{Ni}(\text{DMG})_2$ was cited by Godycki and Rundle as evidence for metal-metal bonding. Yamada and Tsachida (88,89) studied the dichroism of several of the vic-dioxime chelates by a special microscopic technique. Banks and Barnum (10) observed the dichroism of several nickel(II)-vic-dioximes and noted that where the metal-metal distance is long, e.g., nickel heptoxime, the crystals show practically "normal" dichroism. $\text{Ni}(\text{EMG})_2$ was examined microscopically by Anderson (3) and found to show "normal" dichroism which he stated would be expected since no metal-metal bonding can occur in this chelate.

In 1957 Rundle (72) described a molecular orbital scheme for metal-metal bonding in $\text{Ni}(\text{DMG})_2$. The dsp^2 square planar bonds lie in the xy plane. Extending along the z axis, above and below the plane of the molecule is the $3d_{z^2}$ -orbital, which contains two non-bonding electrons, and the $4p_z$ -orbital, which is empty. In forming a dimer two molecules of $\text{Ni}(\text{DMG})_2$ approach along their z axes and form a Ni-Ni bond. The two $3d_{z^2}$ -orbitals combine to form an a_{2u} bonding orbital and an a_{1g}^* anti-bonding orbital. Similarly, the two $4p_z$ -orbitals combine to form an a_{2u} bonding orbital and an a_{1g}^* anti-bonding orbital. The four electrons will then be in the

first two a_{2u} and the a_{1g}^* molecular orbitals, but since one of these orbitals is bonding and the other anti-bonding, there is no net decrease in energy and therefore, no bonding. However, in order to decrease electron repulsions, Rundle suggested that electrons may be partially promoted from the a_{1g}^* to the empty a_{2u} orbital. This process is enhanced somewhat because it results in weak Ni-Ni bonds. Rundle termed this phenomenon "configuration interaction".

Based primarily on their solid state spectral studies, other researchers (90,60,14,4) have challenged Godycki and Rundles' assumption that the dichroic character of the metal-vic-dioximes is evidence for metal-metal bonding.

Anex and Krist (4) have criticized earlier polarized single-crystal spectral studies. These spectroscopists claim that very thin crystals are required to obtain reliable absorption spectra. They used a special microspectrophotometer and obtained well-resolved, polarized, single-crystal spectra for $Ni(DMG)_2$, $Ni(EMG)_2$, and $Ni(Heptox)_2$. The crystals were oriented in the optical path of the instrument by means of a goniometer.

According to Anex and Krist, crystalline $Ni(EMG)_2$ may be taken to represent the "oriented-gas model" for the chelates they studied. These workers treated their solid state spectral data and obtained "equivalent solution spectra" for comparison. They found that a relationship existed between the position of

the lowest energy out-of-plane solid absorption band (that is, the color band described earlier) and the interplanar spacing of the crystalline metal-vic-dioximes much like that of Banks and Barnum (10). Anex and Krist also found a relationship between the intensity of the color band and the interplanar spacing. They concluded that with solid state formation, there is a corresponding intensity loss in the higher energy region of the spectra of the chelates studied which is associated with "chain formation" and not merely with the solid state in general. Thus, a single-molecule origin for the color band has been found which Anex and Krist have traced to a charge-transfer transition.

Anex and Krist have associated the color band with the ($d_{z^2}, \sigma \rightarrow p_z, \pi^*$) metal to ligand charge transfer transition. They suggest that on solid state formation the energy perturbation of the color band arises from ground-state destabilization of the d_{z^2} orbital by similar filled orbitals in adjacent molecules. The authors summarized the available evidence for metal-metal interaction as follows:

1. There is nothing "unusual" about bands being polarized perpendicular to the molecular plane if one is dealing with other than strictly p_z molecular orbitals.
2. The "column-stacking" and low solubility of many square-planar complexes may be favored by electrostatic and packing considerations, regardless of

any metal-metal effects.

3. The striking optical properties of $\text{Ni}(\text{DMG})_2$ may be a side effect of the stacking, not a necessary consequence of it, and could in fact reflect antibonding, instead of, or as well as, bonding effects.

Ingraham (52) has reported a molecular orbital calculation on $\text{Ni}(\text{DMG})_2$. His findings support those of Anex and Krist regarding the possibilities of Ni-Ni interactions, in that they are slight in the ground state but may occur in some excited states. Anex and Krist, however, have pointed out that the calculations were based on band assignments for the lowest energy solution and solid state bands which are incompatible with their assignments.

Recently, there has been some interest in the conductivity properties of the d^8 metal complexes. Collman and coworkers (75,68) have discussed the possibility of a one-dimensional polymeric arrangement of metal atoms in these compounds resulting in unique solid state properties, including anisotropic conductivity and photoconductivity. They have verified the anisotropic electron transport in single crystals of the dicarbonylpentan-2,4-dionates of iridium and rhodium and of Magnus salt, $[\text{Pt}(\text{NH}_3)_4]^{2+}[\text{PtCl}_4]^{2-}$ and the related complex, $[\text{Pt}(\text{NH}_3)_4]^{2+}[\text{PdCl}_4]^{2-}$. They found the conductivity along the needle axis of the iridium compound to be 500 times greater than that perpendicular to this axis.

The longitudinal conductivities were found to be 10^{-5} ohm⁻¹ cm⁻¹ for the iridium complex and 2.5×10^{-4} ohm⁻¹ cm⁻¹ for the platinum complex at 25°C. These results provide definite experimental evidence for the hypothesis of Rundle (72) and of Miller (60) that adjacent d and p orbitals in chains of metal atoms will overlap to form delocalized band-type orbitals either in ground or excited states.

The above compounds are similar to the vic-dioxime chelates of nickel, palladium, and platinum in that the metal atoms are in square planar arrangements and chains of metal atoms form in the crystalline state with interatomic distances of about 3.25Å.

Recently, Rao and his associates (17) measured the electrical conductivities of Ni(DMG)₂, Ni(α-Furil)₂, Ni(α-Benzil)₂, and Pd(DMG)₂ as a function of temperature. The samples were pelletized under pressure (ca. 2000 lb./in.²) with thin platinum electrodes in contact on either side. Table 5 summarizes the direct current electrical conductivities found for the metal-vic-dioximes and Magnus salt as determined by these researchers.

The resistivities of the metal-vic-dioximes are noted to be high compared to those of known semiconductors (pure silicon has a conductivity of about 10^{-5} ohm⁻¹ cm⁻¹). However, a plot of the logarithm of the conductivity versus the reciprocal of the absolute temperature for Pd(DMG)₂ did show the

Table 5. Direct current electrical conductivities of some polymeric coordination compounds

Compound	Temp. °C	Conductivity ohm ⁻¹ cm ⁻¹	Activation energy eV
Ni(DMG) ₂	50	6.3x10 ⁻¹⁵	----
Ni(α-Furil) ₂	250	1.0x10 ⁻¹¹	1.53
Ni(α-Benzil) ₂	250	7.1x10 ⁻¹⁴	1.78
Pd(DMG) ₂	100	8.9x10 ⁻¹²	0.55
[Pt(NH ₃) ₄] ²⁺ [PtCl ₄] ²⁻	100	4.5x10 ⁻⁶	0.11

behavior of a semiconductor. These workers did not report any single crystal conductivity measurements.

For a more complete history of the chemistry of the metal-vic-dioximes, the reader is referred to the reviews of Banks (5,6). Also, Dyrssen (35) has written a review of the coordination chemistry of the metal-vic-dioximes.

The analytical applications of the vic-dioximes are well documented, and the reviews of Diehl (33), Banks (5,6), Beamish (15), and Welcher (83) are recommended to the interested reader.

A monograph on the chemistry of the vic-dioximes is currently in press (30).

III. REAGENTS

A. vic-Dioximes

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

Ethylmethylglyoxime was prepared by the oximation of the Eastman product, 2,3-pentanedione by N. Wilcox of this Laboratory following the procedure of Bryant and Smith (23).

Nioxime and heptoxime were prepared by other workers of this Laboratory. Each one was recrystallized once from a water-alcohol solution. Nioxime was prepared using the procedures of Rauh et al. (69), Geissman and Schlatter (46), and of Hach, Banks, and Diehl (48). Heptoxime was prepared by the method of Vander Haar, Voter, and Banks (80).

3-Methylnioxime, 4-methylnioxime, and 4-isopropylnioxime were prepared in this Laboratory by J. Richard and D. Hooker. The procedures used are described by Banks, Hooker, and Richard (11). The 4-methylnioxime was recrystallized once from a water-ethanol solution. Due to a limited supply of material, the 3-methylnioxime and 4-isopropylnioxime were used without further purification. The melting points of both were determined and found to be within one degree of the literature values.

B. Metal-vic-Dioximes

The metal-vic-dioximes were prepared following analytical procedures where available.

$\text{Ni}(\text{DMG})_2$ was prepared following the procedure of Diehl (33).

$\text{Ni}(\text{Niox})_2$ was prepared according to the procedure of Voter, Banks, and Diehl (81b) and was recrystallized from pyridine.

$\text{Ni}(\text{Heptox})_2$ was prepared by the procedure of Voter and Banks (81a).

$\text{Ni}(3\text{-MeNiox})_2$, $\text{Ni}(4\text{-MeNiox})_2$, and $\text{Ni}(4\text{-IsopNiox})_2$ were prepared by the method of Hooker (51).

All of the above chelates were washed repeatedly with cold ethanol and hot water and dried in an oven at 110°C before using.

Radioactive nickel-63 obtained from the Oak Ridge National Laboratory was used to prepare "tagged" chelates of the above.

$\text{Ni}(\text{EMG})_2$ was prepared by J. Caton of this Laboratory and used without further purification.

$\text{Pd}(\text{DMG})_2$ was prepared according to the analytical procedure of Beamish (15, p. 286) and was washed repeatedly with cold and hot water and dried at 110°C overnight.

$\text{Pt}(\text{DMG})_2$ was prepared following the procedure of Cooper (32), recrystallized from chloroform, washed with hot water, and dried at 110°C for two hours.

C. Other Reagents

n-Heptane was Matheson Coleman and Bell "Chromatoquality Reagent" (99+ mol %).

Carbon tetrachloride and 1,4-dioxane were 'Baker Analyzed' reagents.

Chloroform of reagent-grade quality was obtained from Allied Chemical Company.

PPO, 2,5-diphenyloxazole, was obtained from Packard Instrument Company.

POPOP, p-bis[2-(5-phenyloxazolyl)]-benzene, was obtained from Pilot Chemicals, Incorporated.

Hexachloroethane was obtained from Aldrich Chemical Company.

All other reagents used were of reagent-grade quality.

IV. EXPERIMENTAL

A. Determination of the Solubilities of the Ni(II)-vic-Dioximes in Chloroform and in n-Heptane1. General considerations

The solubilities of many of the metal-vic-dioximes have been determined in different solvents (36). It has been found that the Ni(II)- and Pd(II)-vic-dioximes are quite soluble in chloroform relative to other common organic solvents (36,73). Consequently, chloroform has been used extensively as an extractant for these chelates. Typically, nickel or palladium is complexed with a vic-dioxime, extracted into chloroform and the absorbance of the chloroform phase is measured spectrophotometrically at a suitable wavelength (5). Hooker (51) found the solubility of Ni(3-MeNiox)₂, Ni(4-MeNiox)₂, and Ni(4-IsopNiox)₂ in chloroform to be 39 ± 5, 16 ± 2, and 200 ± 20 g/l, respectively. These values seem unreasonably high when compared to reported values of other Ni(II)-dioximes.

The solubilities of a series of Ni(II)-vic-dioxime chelates were determined in chloroform at 25°C. These solubilities should be useful in determining how the character of the ligand influences solubility.

It has been suggested that the solubilities of the Ni(II)-vic-dioximes in n-heptane might be indicative of their relative crystal energies (6). Further, if Ni-Ni bonding is important in stabilizing the crystals of these chelates, a

correlation between Ni-Ni distance in the solid state and the solubility in n-heptane might be expected. The solubilities of a series of Ni(II)-vic-dioximes which are isomorphous with Ni(DMG)₂ were determined to test this hypothesis.

2. Apparatus and procedures

a. Solubility in chloroform Saturated solutions of the Ni(II)-vic-dioximes were prepared by adding an excess of chelate to chloroform. The solutions were allowed to equilibrate for at least 24 hours in a constant temperature bath set at $25.0 \pm 0.05^{\circ}\text{C}$. The solutions were shaken periodically by hand. Aliquots of the saturated solutions were filtered through filter paper in a room which was maintained in the temperature range of 24 to 26°C . Care was taken to avoid evaporation losses. Measured volumes of the filtered, saturated solutions were immediately diluted with chloroform to a known volume. The absorbances of the solutions were then measured spectrophotometrically in quartz cells with a Beckman DU spectrophotometer equipped with a hydrogen source and a photomultiplier attachment. The concentrations of the solutions were determined from a standard curve prepared from absorbance readings of dilutions of a standard solution of the chelate being studied. Known amounts of the chelate were weighed out with the aid of a Cahn electrobalance, dissolved in chloroform, and diluted to the calibration mark of a volumetric flask with more chloroform. Saturated solutions of Ni(DMG)₂ prepared at 10° and 40°C and then equilibrated to

25°C as described above were found to give the same results within experimental error, indicating that equilibrium was established by the saturation procedure.

b. Solubility in n-heptane Saturated solutions of the Ni(II)-vic-dioximes were prepared by adding an excess of the chelate to be studied to n-heptane and shaking the solutions in a constant temperature bath for at least 24 hours with a Burrell "wrist action" shaker. The temperature was maintained at $25^{\circ} \pm 0.05^{\circ}\text{C}$ in the bath. Aliquots of the saturated solutions were filtered through Schleicher and Schuell No. 589 Red Ribbon filter paper (for crystalline materials) which was supported by a funnel with a Teflon stopcock in its stem. The stopcock allowed the filtration to be stopped when the filtrate just reached the calibration mark on a volumetric flask placed beneath the stem. Care was taken to avoid evaporation losses. The room was maintained at $25^{\circ} \pm 1^{\circ}\text{C}$. The measured volumes of the filtered saturated solutions were then transferred to beakers quantitatively by washing the filtrates out of the collection flasks with dioxane. The solutions in the beakers were placed on a hot plate and evaporated just to dryness by heating gently and passing a slow stream of air over them. Care was taken not to "bake" the chelate residue. The remaining chelate residue was analyzed either by an atomic absorption procedure or a spectrophotometric procedure.

The atomic absorption procedure consisted of dissolving the residue in a known volume of dioxane. The volume was always less than the original volume of saturated solution taken, effecting a concentration step to get the concentration of chelate up to a measurable level. The "concentrated" dioxane solution was then analyzed by measuring the atomic absorbance of nickel at $232.4 \text{ m}\mu$ with a Perkin-Elmer 303 atomic absorption spectrophotometer. An air-acetylene flame was employed. A Sargent strip chart recorder was used to record the instrumental response during the measurements. The solution concentrations were determined from a standard curve prepared from absorbance readings taken of a standard solution of the complex being determined. The standards were treated the same as the samples beginning with the evaporation step. The standard solution was prepared by weighing out a known amount of the chelate on a Cahn electrobalance, and, after transferring the weighed portion to a volumetric flask, it was dissolved in dioxane and diluted to volume with the same solvent. It was found that the standard solution had to be freshly prepared for each experiment. Evidently, adsorption losses onto glass are quite significant for dilute solutions of the Ni(II)-vic-dioximes in organic solvents.

A spectrophotometric procedure was used to determine the solubility of $\text{Ni}(\beta\text{-MeNiox})_2$ in n-heptane. The procedure was similar to that of the atomic absorption procedure except

that the chelate residue was redissolved in chloroform and the absorbance of the chelate was measured at 331.5 m μ using a Beckman DU spectrophotometer.

The spectrophotometric procedure of Alexander et al. (1) was employed for the determination of Ni(Heptox)₂, Ni(4-MeNiox)₂, and Ni(4-IsopNiox)₂. The atomic absorption procedure was followed through the evaporation step. The residue was then transferred quantitatively to a separatory funnel with 15 ml of chloroform. The complex was destroyed with dilute hydrochloric acid and the Ni²⁺ extracted into the aqueous layer. The color was developed with sodium diethyldithiocarbamate in iso-amyl alcohol, and the absorbance read at 324 m μ with a Beckman DU spectrophotometer. The solution concentrations were determined from a standard curve prepared from dilutions of a standard nickel solution. The nickel solution was prepared by dissolving pure nickel shot ('Baker Analyzed') in hydrochloric acid. The solution was standardized using the EDTA titrimetric method of Flaschka (39).

3. Experimental results

a. Solubility in chloroform Table 6 gives the results of the solubility measurements of the Ni(II)-vic-dioximes in chloroform as found in this work and as found by others. The solubilities reported for this work are the average of at least two determinations.

b. Solubility in n-heptane Table 7 reports the results of the solubility measurements of the Ni(II)-vic-

Table 6. Molar solubilities of some Ni(II)-vic-dioximes in chloroform at 25°C

Chelate	Factor ^a	Determinator			
		This work	Fleischer ^b	Banks & Barnum ^c	Hooker ^d
Ni(DMG) ₂	10 ⁴	4.89±0.03	4.62±0.03	5.5±0.3	
Ni(Niox) ₂	10 ⁵	6.72±0.14		6.7±0.8	
Ni(Heptox) ₂	10 ³	5.91±0.05		5.6±0.1	
Ni(3-MeNiox) ₂	10 ³	5.87±0.07			106
Ni(4-MeNiox) ₂	10 ³	6.43±0.07			43
Ni(4-IsopNiox) ₂	10 ³	9.25±0.05			470

^aValues in their respective horizontal rows of the table have been multiplied by this factor.

^bReference (40).

^cReference (9).

^dReference (51).

dioximes in n-heptane at 25°C. The atomic absorption and the spectrophotometric values have been averaged together where both methods were used to determine the solubility

Table 7. Molar solubilities of some Ni(II)-vic-dioximes in n-heptane at 25°C

Ni(II)chelate	Solubility	Number of determinations
DMG	$2.37(\pm 0.20) \times 10^{-7}$	14
Niox	$3.62(\pm 1.73) \times 10^{-8}$	10
Heptox	$1.38(\pm 0.16) \times 10^{-6}$	10
3-MeNiox	$4.87(\pm 0.96) \times 10^{-6}$	13
4-MeNiox	$1.17(\pm 0.11) \times 10^{-6}$	9
4-IsopNiox	$1.82(\pm 0.27) \times 10^{-6}$	8

B. Determination of the Thermodynamic

Constants for the Dissolution of the Metal-vic-Dioximes in
Non-coordinating Solvents

1. Theory

The heat of solution of a compound is equal to the sum of the heat of vaporization and the heat of solvation. In order for heats of solution of a series of compounds to be indicative of their relative crystal energies, the heats of vaporization and the heats of solvation must be "regular" throughout the series. That is, no "unusual" contributions can be made

to the heat of vaporization or solvation of any member of the series. If one member of the series underwent some molecular rearrangement upon dissolution that the other series members did not undergo, its heat of fusion would not be "regular" with respect to the series. Further, there should be little or no solvent-solute interaction, or the degree of interaction should be the same for all members of the series. Any interaction of the solvent with the solute will tend to decrease the over-all heat measured.

Fleischer (40) and Anderson (3) have measured the heats of solution of some metal-vic-dioximes in various solvents. They have suggested that the solvents carbon tetrachloride and n-heptane give rise to no unusual solvent-solute effects. They have taken the difference in the heats of solution in these solvents to be a measure of the difference in the crystal energies of the metal-vic-dioximes.

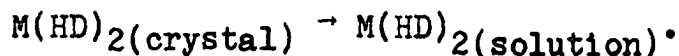
The heats of solution of a series of Ni(II)-vic-dioxime chelates which are isomorphous with Ni(DMG)₂ were measured in n-heptane by the solubility dependence on temperature method. The variation in the heat of solution with change in the aliphatic character of the ligand might give an indication of the importance of the ligand in stabilizing the crystal.

The heat of solution of Ni(EMG)₂ in n-heptane was determined by Anderson (3) to be 5.6 kcal/mole. The solubility values found by Anderson for Ni(EMG)₂ appeared to be quite low when compared to those of the other Ni(II)-vic-dioximes.

Therefore, the heat of solution of $\text{Ni}(\text{EMG})_2$ in n-heptane was redetermined.

The heats of solution of $\text{Ni}(\text{DMG})_2$, $\text{Pd}(\text{DMG})_2$ and $\text{Pt}(\text{DMG})_2$ were determined in carbon tetrachloride to measure what effect the metal has on crystal energy.

The dissolution of a metal-vic-dioxime in carbon tetrachloride or n-heptane may be represented by the equation



The van't Hoff reaction isobar defines the temperature coefficient of $\ln X_2$ in terms of the heat of solution, ΔH° , and the temperature T for this process as,

$$\frac{\partial \ln X_2}{\partial T} = \frac{\Delta H^\circ}{RT^2} \quad (1)$$

where X_2 is the mole fraction of solute in the saturated solution (50). For exact integration of Equation 1, ΔH° must be known as a function of T . However, when the temperature interval considered is not very large, ΔH° may be considered constant over the interval. Equation 1 may be obtained in the forms

$$d \ln X_2 = \frac{\Delta H^\circ}{RT^2} dT \quad (2)$$

and

$$\ln X_2 = \frac{\Delta H^\circ}{RT} + C \quad (3)$$

C is an integration constant which can be evaluated for the process by substituting a known value of X_2 at some given

temperature. According to Equation 3, a plot of $\log_{10}X_2$ vs $1/T$ should be a straight line with slope equal to $-\Delta H^\circ/2.303R$, and hence ΔH° can be determined as follows

$$\Delta H^\circ = -2.303R(\text{slope}) \quad (4)$$

where R is the gas constant equal to $1.987 \text{ cal deg}^{-1}\text{mol}^{-1}$.

The standard state for each solute in the calculation was the mole fraction one and 298.16°K . The Gibbs free energy change and the entropy change were calculated from the following expressions:

$$\Delta G^\circ = -RT\ln X_2 \quad (5)$$

$$\Delta S^\circ = (\Delta H^\circ - \Delta G^\circ)/T \quad (6)$$

The activity coefficient has been assumed to be equal to one, and the heat of dilution has been assumed to be negligible for these very dilute solutions.

2. Apparatus and procedures

a. Ni(II)-vic-dioximes in n-heptane Ni(II)-vic-dioximes were prepared using a $0.1M$ $\text{Ni}(\text{NO}_3)_2$ solution, to which suitable amounts of radioactive nickel-63 were added, according to the procedures described in the REAGENTS section. Nickel-63 emits low energy β -particles (0.067 Mev) and has a half-life of 92 years. Due to the absorption of low energy β -particles by small amounts of matter, a liquid scintillation counting procedure was used.

Saturated n-heptane solutions of the "tagged" chelates were prepared. The solutions were equilibrated in a constant

temperature bath for at least 24 hours. The temperature was held constant to within $\pm 0.1^{\circ}\text{C}$. The solutions were shaken intermittently by means of a mechanical shaker. The solutions were equilibrated in a specially designed apparatus diagramed in Figure 3a. When the saturated solution was sampled, the special pipette (Figure 3b) replaced the cap on the filtering stem and a positive pressure was applied above the saturated solution. The pipette was maintained at a temperature above the saturated solution by placing a specific voltage across the resistance wire. The filtered sample (1 or 2 ml) was then transferred to a previously weighed screw-capped counting vial containing 15 ml of the liquid scintillator. The sample was reweighed, and then its activity was measured with a Beckman LS200B Liquid Scintillation System.

The scintillator solution contained 113.6 g naphthalene, 4.73 g PPO, 0.047 g POPOP dissolved in 950 ml of dioxane in all cases except $\text{Ni}(\text{NiOx})_2$. All the operations involving the scintillator solution were carried out in either the dark or indirect light to prevent photoactivation and subsequent phosphorescent background.

A minimum of 4000 counts above background was accumulated for each sample. This represents a statistical counting error of $\pm 3\%$ at the 95% confidence level.

The background-corrected sample activities were normalized and taken as a measure of the relative solubilities of

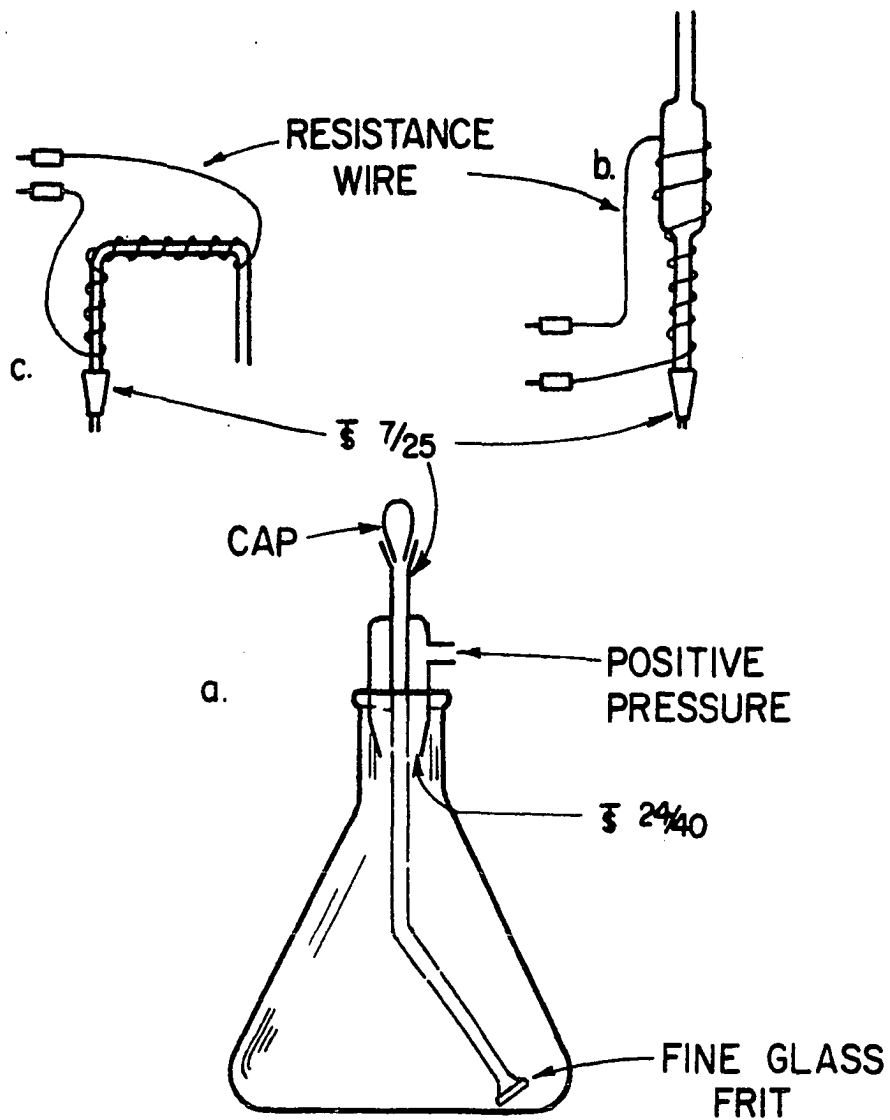


Figure 3. Apparatus used for sampling saturated solutions

Ni(II)-vic-dioximes. This assumes that instrumental and chemical conditions were the same for all measurements. The Beckman LS-200B Liquid Scintillation System operating conditions and instrumental response are reported to be reproducible within the limits of error of this experiment (16). The samples were prepared with the same amounts of saturated solution and scintillator solution in each case. The activity of a stock dioxane solution of "tagged" Ni(4-IsopNiox)₂ was measured at intervals throughout the experiment and was found to be reproducible to within $\pm 3\%$.

A scintillator solution containing 0.055 g POPOP and 4.0 g PPO dissolved in one liter of toluene was used for Ni(Niox)₂ in the above procedure. A standard solution of "tagged" Ni(Niox)₂ was prepared by weighing out a known amount of the chelate and dissolving in toluene to make 500 ml of solution. The "tagged" Ni(Niox)₂ used for the saturated n-heptane solution and the standard solution came from the same preparation of the chelate. A standard curve was prepared from dilutions of the standard solution. Absolute solubility values for Ni(Niox)₂ in n-heptane were then obtained using the standard curve. Activity measurements of a 0.5-ml aliquot of the standard solution taken periodically throughout the experiment were found to be reproducible to within $\pm 3\%$.

Ni(EMG)₂ which was purified by vacuum sublimation (at approximately 160°C and 5×10^{-3} mm Hg pressure) was added to

n-heptane to prepare a saturated solution. The apparatus illustrated in Figure 3 was used for sampling. After equilibrating the $\text{Ni}(\text{EMG})_2$ with n-heptane at a constant temperature by means of a constant temperature bath for 24 hours, samples were taken of the saturated solution by adding enough solution to a 25-ml volumetric flask containing 20 ml of n-heptane to bring the volume to the calibration mark. The absorbance of the resulting solution versus a blank of n-heptane was measured at 265 $\text{m}\mu$ with a Cary 16 spectrophotometer in 1-cm quartz cells.

The absorbances were compared to those of a standard curve prepared by measuring the absorbances of dilutions of a standard solution. The standard solution was prepared by weighing out a known amount of $\text{Ni}(\text{EMG})_2$ with the aid of a Cahn electrobalance. The weighed quantity of $\text{Ni}(\text{EMG})_2$ was dissolved in n-heptane, and diluted to the calibration mark in a 500-ml volumetric flask with additional n-heptane.

b. $\text{Pd}(\text{DMG})_2$ and $\text{Pt}(\text{DMG})_2$ in carbon tetrachloride

$\text{Pd}(\text{DMG})_2$ was placed in a glass column designed after that of Dyrssen and Tyrrell (37). Carbon tetrachloride was added to the 10-mm i.d. glass column where it was forced through a 5-cm column of the chelate and then a fine glass frit by a 15 lb/in^2 head pressure. Saturation equilibrium was achieved by one pass of solvent through the column. The column was thermostated by circulating constant-temperature ($\pm 0.05^\circ\text{C}$)

water through a surrounding water jacket. A small diameter glass tube was used for the delivery stem to achieve a small "dead-volume" below the glass frit. The samples were collected in volumetric flasks covered with a strip of Teflon tape fitted around the delivery stem to reduce evaporation losses. The samples were then quantitatively transferred to beakers using a chloroform wash solution and the solvent was evaporated. The chelate was then destroyed with a boiling nitric acid-hydrogen peroxide mixture. Concentrated hydrochloric acid was added, and the mixture was evaporated to dryness to remove the nitric acid. The remaining PdCl_2 was dissolved in 1 N HCl and analyzed according to the p-nitro-sodimethylaniline spectrophotometric procedure of Overholser and Yoe (65) using either a Beckman DU or a Cary 16 spectrophotometer. The concentrations of the saturated solutions were determined from a standard curve prepared by taking aliquots of a standard chloroform solution of $\text{Pd}(\text{DMG})_2$ and treating them by the same procedure as the saturated solutions.

A saturated solution of $\text{Pt}(\text{DMG})_2$ was prepared by adding an excess of chelate to carbon tetrachloride. The solution was contained in the vessel described in Figure 3a. The vessel was placed in a constant temperature bath ($\pm 0.05^\circ\text{C}$) and the solution was stirred by a Teflon encased iron bar which was rotated by a magnetic stirrer beneath the bath. The sampling procedure was similar to that of the Ni(II)-vic-

dioximes in n-heptane, except that the delivery stem shown in Figure 3c was used to transfer the filtered, saturated solution into a volumetric flask. A volume correction was made on samples collected at temperatures above 25°C for the expansion of the carbon tetrachloride.

An extraction procedure based on a paper by Burger and Dyrssen (24) was developed and used to analyze the saturated solutions. In the procedure a sample of the saturated solution was taken, five milliliters of chloroform were used to transfer the sample to a glass-stoppered flask, and then five milliliters of 1M NaOH were used to extract the chelate. The absorbance of the aqueous phase was measured versus a blank at 285 m μ with a Cary 16 spectrophotometer. The concentrations were determined by comparing the absorbance readings to a standard curve prepared from a standard chloroform solution of Pt(DMG)₂. Aliquots of less than five milliliters of the standard solution were taken and diluted to a total of five milliliters with chloroform, a volume of carbon tetrachloride equal to that of the saturated samples was added, and then the mixture was extracted and the absorbance measured as above.

3. Experimental results

a. Ni(II)-vic-dioximes in n-heptane The solubility values for Ni(DMG)₂ and Ni(Niox)₂ were found to increase with each sample taken at 25°C during the first few determinations. Subsequent samplings with the same pipet reached a "constant"

value as shown in Figure 4 for $\text{Ni}(\text{Niox})_2$. The constant values were taken as the solubility values for $\text{Ni}(\text{DMG})_2$ and $\text{Ni}(\text{Niox})_2$. The other chelates were found to give constant values after the fourth sample. This phenomenon was attributed to the adsorption of the chelates on the walls of the glassware in the sampling system. As $\text{Ni}(\text{Niox})_2$ is the least soluble of all the chelates studied, this explanation is consistent with the observation that it required the greatest amount of saturated solution to saturate the "adsorption sites" and that samples at higher temperature points required only three samples to reach a "constant" value.

Table 8 summarizes the solubility values for the $\text{Ni}(\text{II})$ -vic-dioximes in n-heptane. All the values, except for $\text{Ni}(\text{Niox})_2$ and $\text{Ni}(\text{EMG})_2$ are relative to the 25°C values given in Table 7.

The logarithm of the mole fraction solubilities of the $\text{Ni}(\text{II})$ -vic-dioximes in n-heptane were plotted versus the reciprocal of the absolute temperature as illustrated in Figures 5 and 6. The heats of solution were calculated from the slopes of the curves using Equation 4. The slopes were determined from plots on two-cycle, not five-cycle, semi-logarithmic paper as shown in Figure 5. Table 9 gives the heat of solution, free energy, and entropy for the $\text{Ni}(\text{II})$ -vic-dioximes for dissolution in n-heptane.

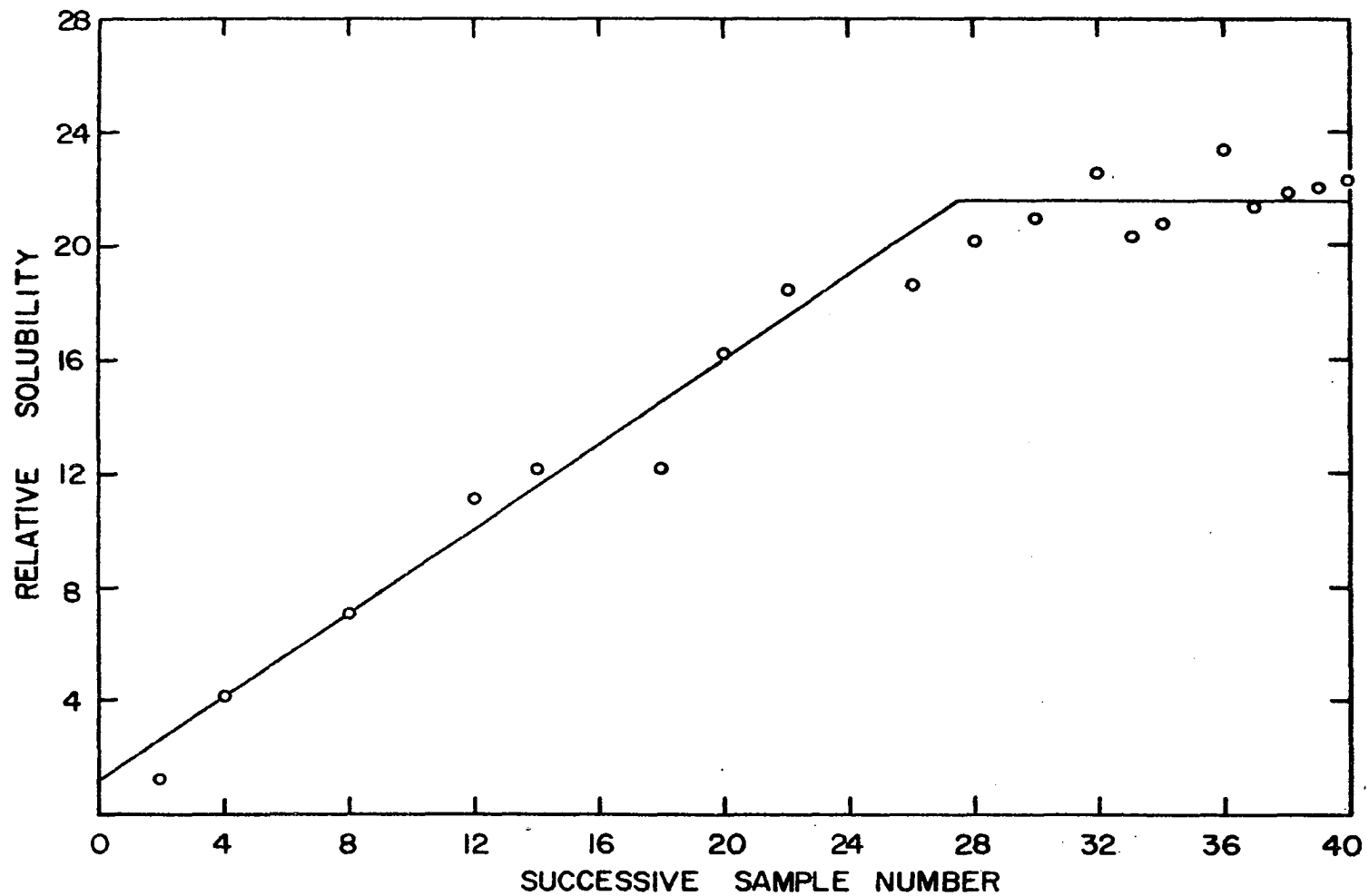


Figure 4. Change in relative solubility of $\text{Ni}(\text{NiOx})_2$ at 25°C with successive sample number

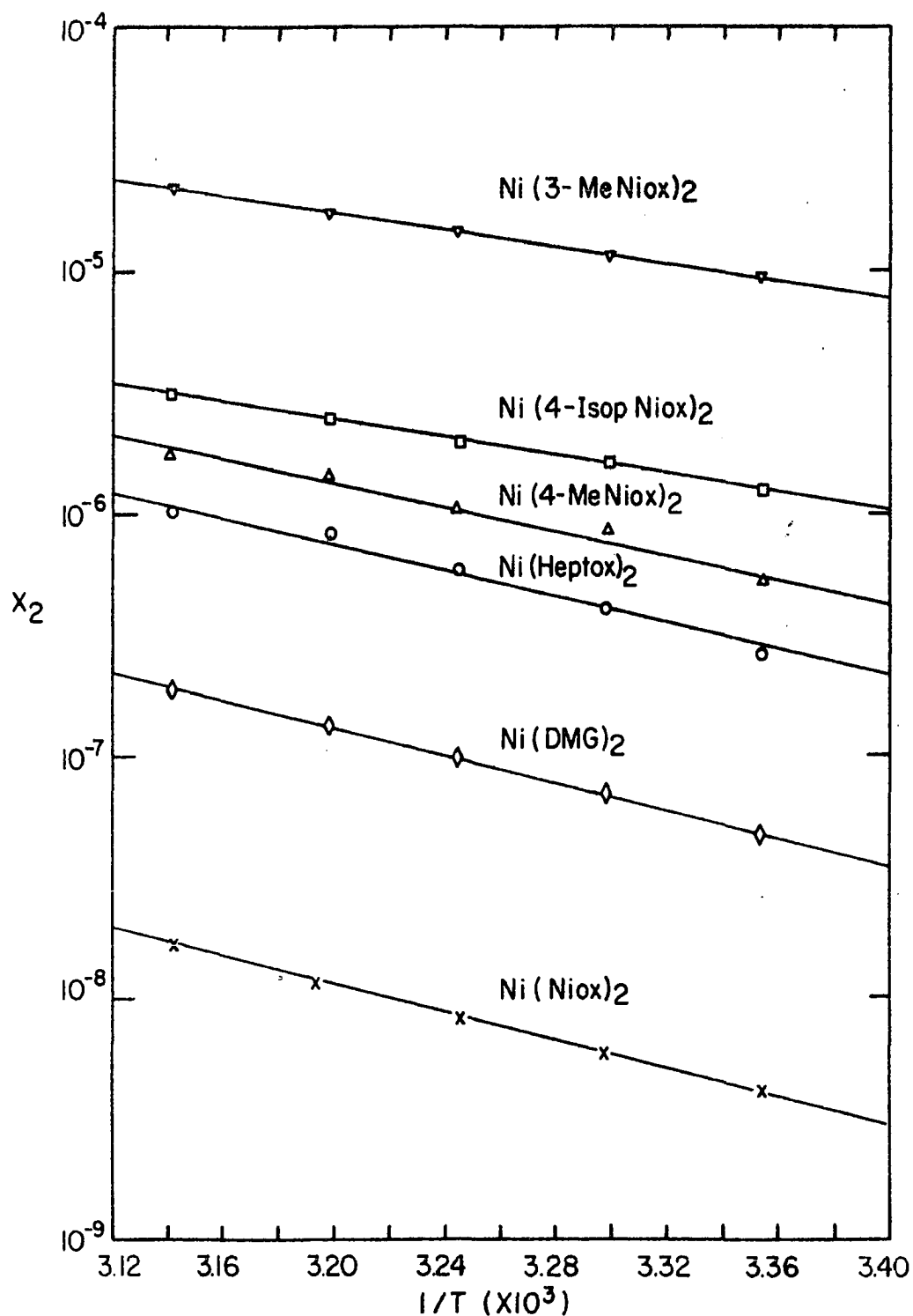


Figure 5. Log mole fraction solute versus the reciprocal of the absolute temperature for some Ni(II)-vic-dioximes in n-heptane

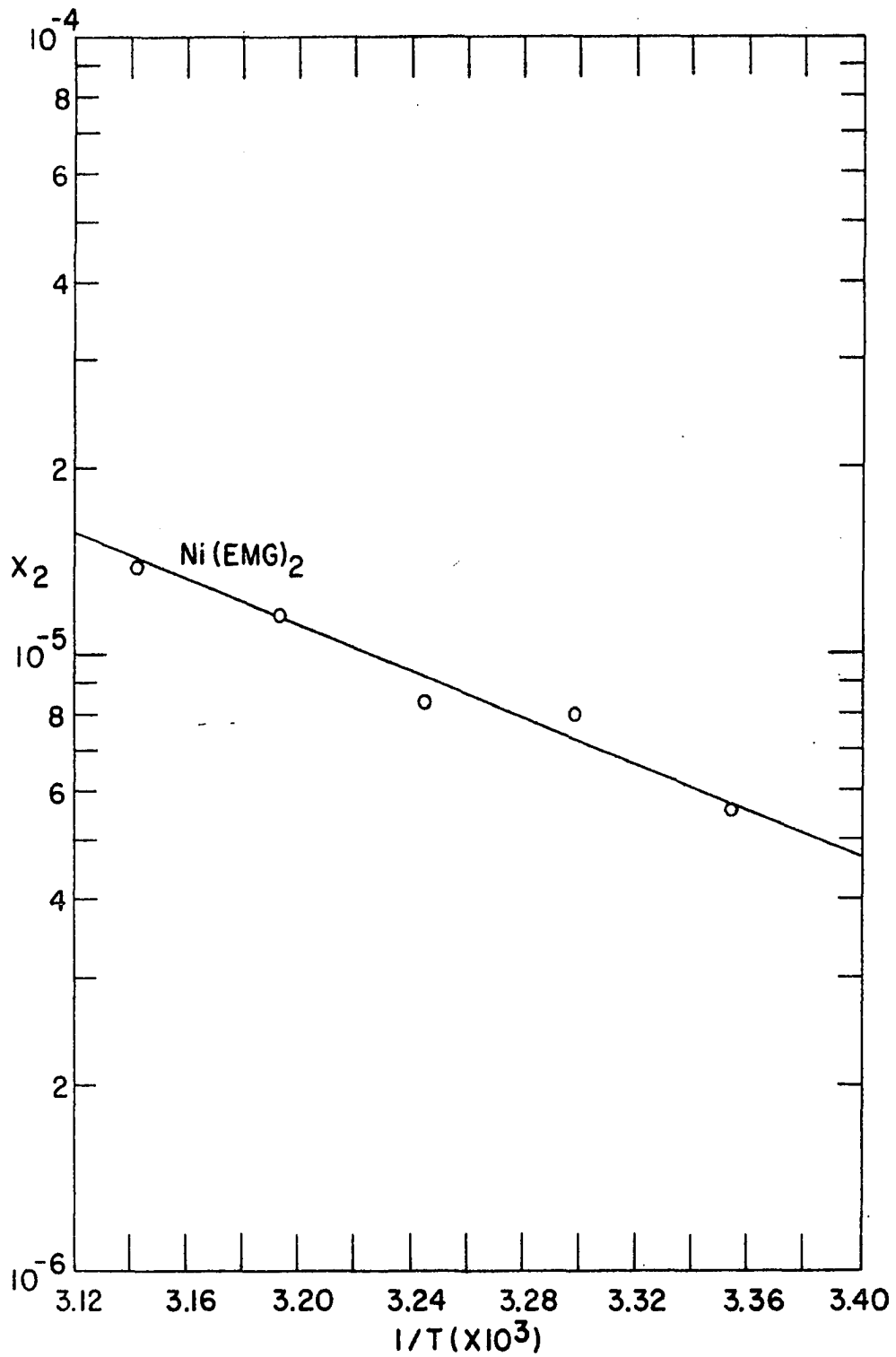


Figure 6. Log mole fraction solute versus the reciprocal of the absolute temperature for $Ni(EMG)_2$ in n-heptane

Table 8. Solubilities of some Ni(II)-vic-dioximes in n-heptane^a

Nickel chelate	-log X ₂ at °C				
	25.09°	30.07°	35.02°	40.03°	45.06°
Niox	8.40	8.24	8.09	7.93	7.78
DMG	7.46	7.30	7.14	7.00	6.85
Heptox	6.69	6.51	6.37	6.19	6.10
3-MeNiox	6.14	6.05	5.94	5.85	5.75
4-MeNiox	6.76	6.54	6.45	6.31	6.21
4-IsopNiox	6.57	6.45	6.37	6.26	6.16
EMG	5.25	5.10	5.08	4.92	4.86

^aValues are relative to 25°C determinations taken from Table 7, except for Ni(Niox)₂ and Ni(EMG)₂ which are absolute values.

Table 9. Thermodynamic constants for the dissolution of some Ni(II)-vic-dioximes in n-heptane^a

Chelate	ΔH°	ΔG°	ΔS°
	(kcal/mole)	(kcal/mole)	(cal/mole deg)
Ni(DMG) ₂	14.1	10.17	13.1
	15.1 ^b	10.15 ^b	16.6 ^b
Ni(Niox) ₂	13.4	11.45	6.5
Ni(Heptox) ₂	13.6	9.13	15.1
Ni(3-MeNiox) ₂	9.3	8.38	3.0
Ni(4-MeNiox) ₂	12.6	9.22	11.3
Ni(4-IsopNiox) ₂	9.5	8.96	1.7
Ni(EMG) ₂	8.6	6.56	7.6
	5.8 ^c	9.19 ^c	-11.4 ^c

^aStandard state taken as mole fraction one and 298.16°K.

^bTaken from Fleischer (40).

^cTaken from Anderson (3).

b. Pd(DMG)₂ and Pt(DMG)₂ in carbon tetrachloride The

solubility values measured for Pd(DMG)₂ and Pt(DMG)₂ are listed in Table 10. The solubilities of Ni(DMG)₂ in carbon tetrachloride were taken from Banks and Anderson (7). Plots of the logarithm of the mole fraction solubility versus the reciprocal of the absolute temperature are shown in Figure 7 for Pd(DMG)₂ and Pt(DMG)₂. The slopes of the curves were used to calculate the heats of solution using Equation 4.

Table 10. Solubilities of Ni(DMG)₂, Pd(DMG)₂, and Pt(DMG)₂ in carbon tetrachloride

Chelate	-log X ₂ at °C					
	25°	30°	33.3°	35°	40°	45°
Ni(DMG) ₂ ^a	6.24		5.92			
Pd(DMG) ₂	6.02	5.91		5.84	5.76	5.67
Pt(DMG) ₂	6.80	6.66		6.56	6.43	6.30

^aValues for Ni(DMG)₂ were taken from Banks and Anderson (7).

Table 11 summarizes the thermodynamic constants for the dissolution of Ni(DMG)₂, Pd(DMG)₂, and Pt(DMG)₂ in carbon tetrachloride.

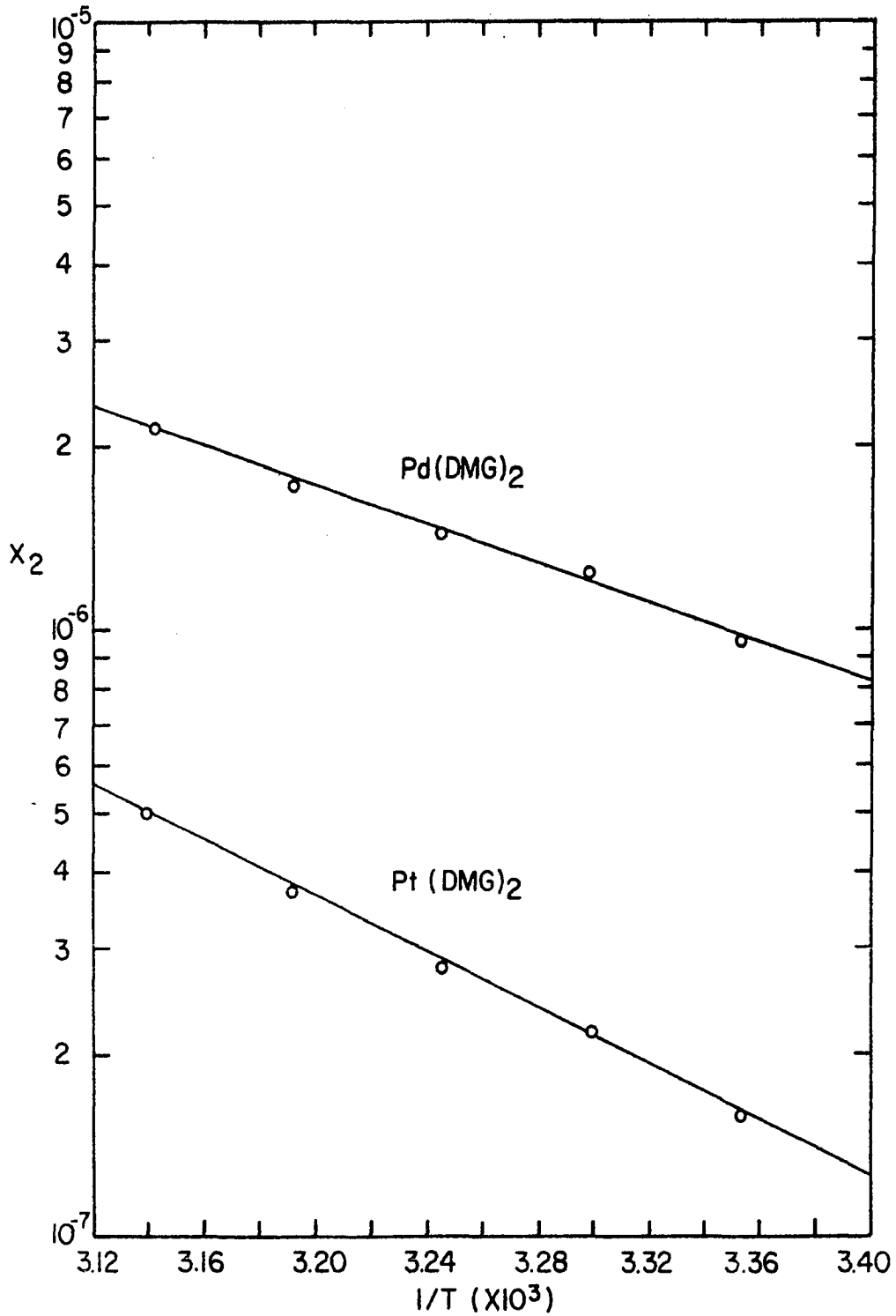


Figure 7. Log mole fraction solute versus the reciprocal of the absolute temperature for $\text{Pd}(\text{DMG})_2$ and $\text{Pt}(\text{DMG})_2$ in carbon tetrachloride

Table 11. Thermodynamic constants for the dissolution of Ni(DMG)₂, Pd(DMG)₂, and Pt(DMG)₂ in carbon tetrachloride^a

Chelate	ΔH° (kcal/mole)	ΔG° (kcal/mole)	ΔS° (cal/mole deg)
Ni(DMG) ₂ ^b	15.3	8.50	22.8
Pd(DMG) ₂	7.4	8.21	-2.7
Pt(DMG) ₂	10.6	9.28	4.4

^aStandard state taken as mole fraction one and 298.16°K.

^bValues for Ni(DMG)₂ taken from Banks and Anderson (7).

C. Gas Phase and Chloroform Solution

Visible and Ultraviolet Spectra of Ni(DMG)₂ and Ni(EMG)₂

1. General considerations

The nickel-vic-dioximes exhibit a color band in their solid state spectra which is not found in their solution spectra.¹ Previous workers have treated the chloroform solution spectra of the nickel-vic-dioximes as being representative of their gas phase spectra (10,14,4). To do this requires that no unusual solvation effects are altering the chloroform solution spectra.

The gas phase visible and ultraviolet spectra of Ni(DMG)₂ and Ni(EMG)₂ were taken to determine if their gas phase spectra are representative of their chloroform solution

¹See the LITERATURE REVIEW for a complete discussion of this phenomenon.

spectra. This experiment should determine the reason the color band is absent in chloroform solution spectra. If the gas phase spectra are representative of the solid phase spectra, then the color band is absent in chloroform solution due to unusual solvation effects. However, if the gas phase spectra approximate the chloroform solution spectra, the color band can be said to be a phenomenon of the solid state, and the assumption of the previous workers is valid.

2. Apparatus and procedures

The gas phase spectra were taken with a Cary 14 spectrophotometer modified by Richard Lynde of this Laboratory. In the experiment the chelate to be studied was placed in a 10-cm cylindrical quartz cell which was evacuated to a pressure of approximately 10^{-3} Torr and sealed off. The cell was placed in the cell compartment of the spectrophotometer and heated by means of a tube furnace. The instrument is of such design that the temperature of the two ends of the cell was kept higher than the center of the cell to prevent condensation of the chelate onto the optical faces. The temperatures of the center and the ends of the cell were monitored by thermocouples adjacent to the cell. A temperature of 240°C for $\text{Ni}(\text{DMG})_2$ and of 194°C for $\text{Ni}(\text{EMG})_2$ was required to obtain a good spectrum. The spectra were corrected for background by subtracting off the absorbance due to the cell.

Chloroform solution spectra of $\text{Ni}(\text{DMG})_2$ and $\text{Ni}(\text{EMG})_2$

were measured with a Cary 14 spectrophotometer.

3. Experimental results

The gas phase and chloroform solution spectra of $\text{Ni}(\text{DMG})_2$ and of $\text{Ni}(\text{EMG})_2$ are shown in Figures 8 and 9, respectively. The gas phase spectra should be considered only qualitatively since no measure of the amount of chelate in the optical path was made. The chelates were noted to have darkened slightly from being heated. However, the sublimate for each of the chelates which condensed on the cooler portion of the cell walls had the same color as the original chelates, indicating that the absorbing vapor was chelate and not a decomposition product. Also, after the gas phase spectra were measured, the sealed cells were heated, and chelate was sublimed onto the optical faces. The visible and ultraviolet spectra of these sublimate were noted to be identical to their respective solid state mull spectra.

D. Infrared Spectra of Some $\text{Ni}(\text{II})$ -vic-Dioximes

1. General considerations

The controversy over the band assignments for the infrared spectra of the metal-vic-dioximes was discussed in the LITERATURE REVIEW.

The infrared spectra of some of the $\text{Ni}(\text{II})$ -vic-dioximes were measured in the 4000 to 1300 cm^{-1} region. This region is where the OH stretching and bending vibrations occur (28). The spectra were taken to determine if the hydrogen bond

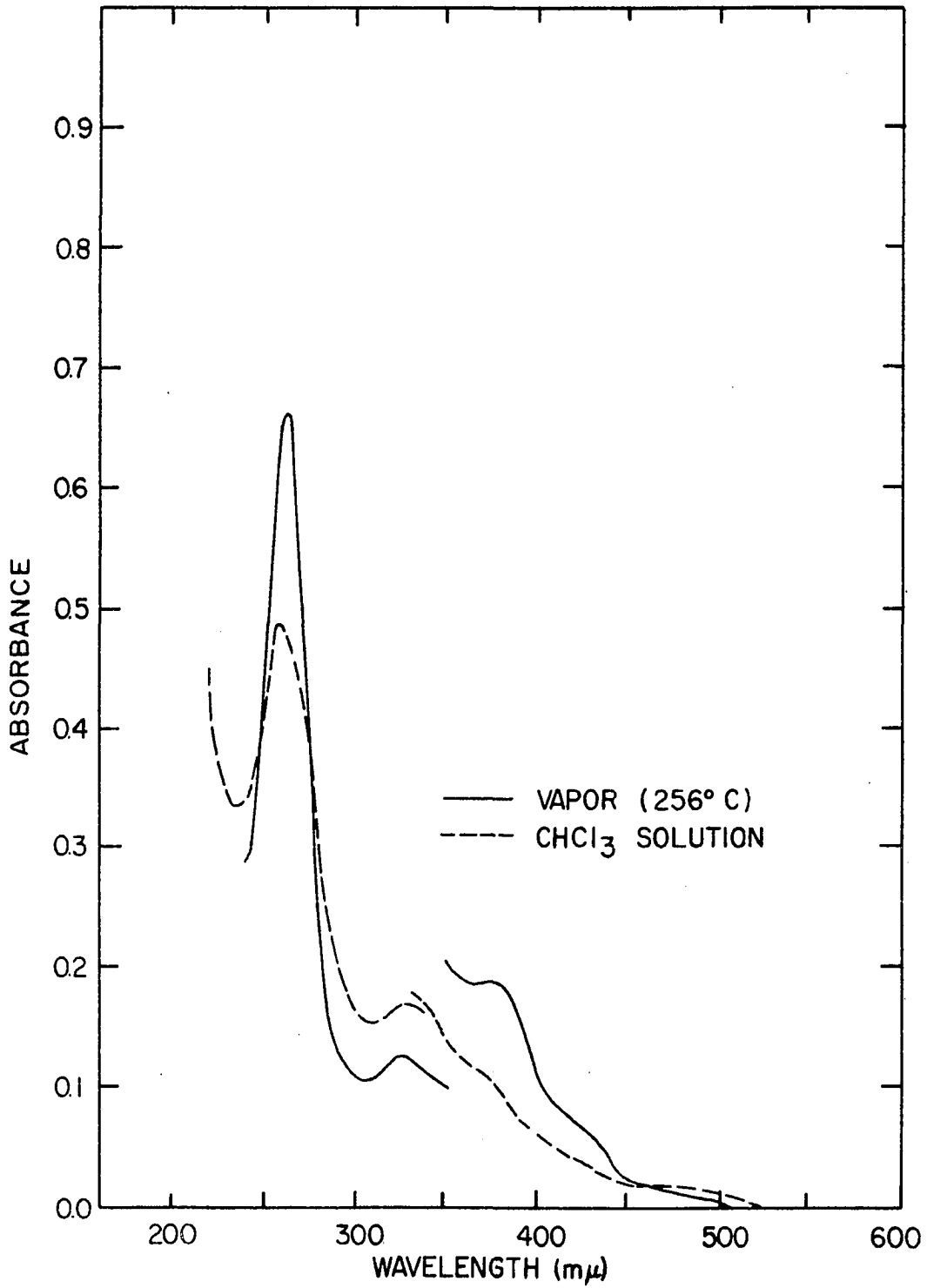


Figure 8. Gas phase and chloroform solution spectra of Ni(DMG)₂

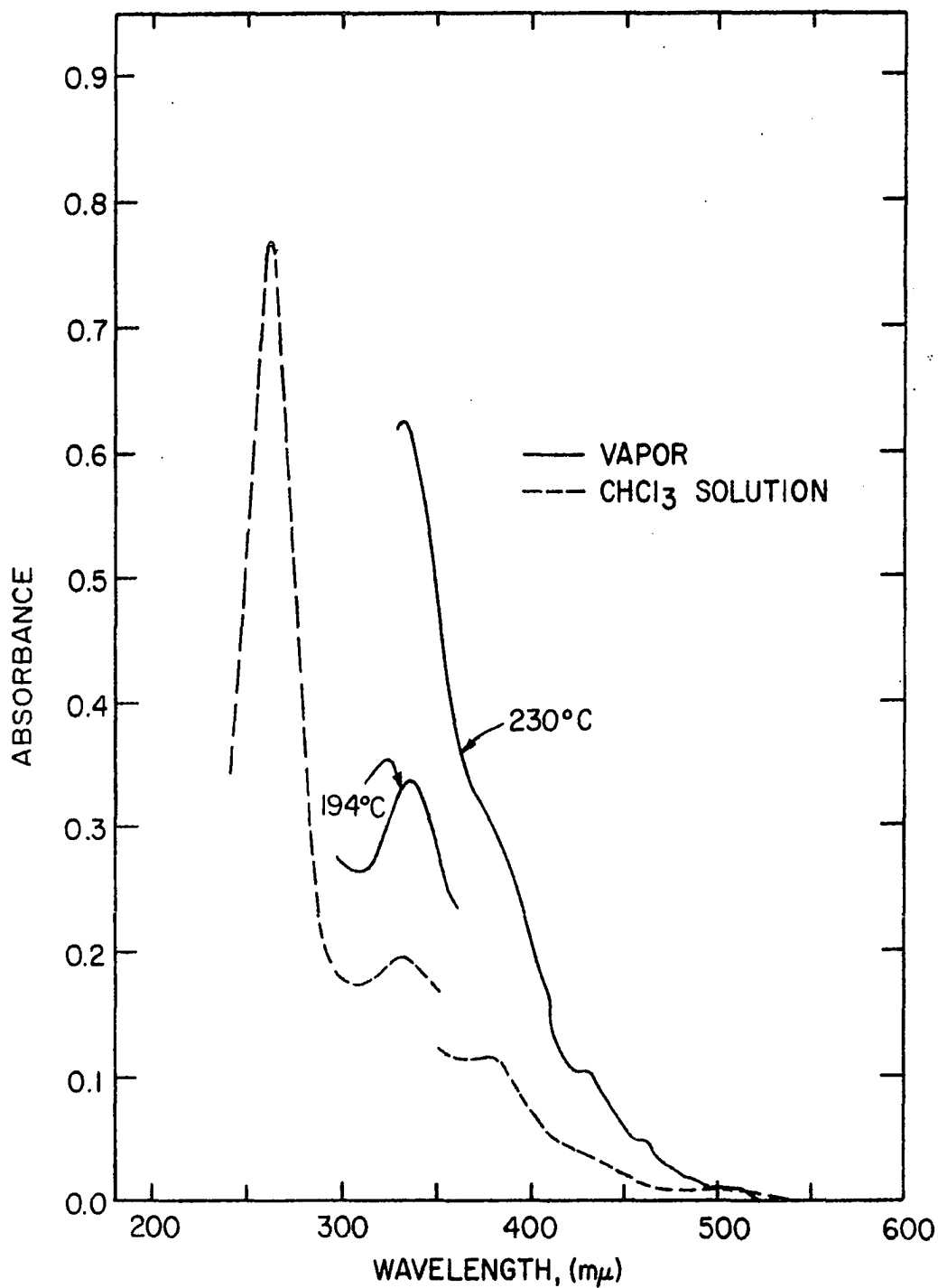


Figure 9. Gas phase and chloroform solution spectra of $\text{Ni}(\text{EMG})_2$

systems of the nickel chelates of the substituted nioximes and of heptoxime are similar to those of $\text{Ni}(\text{DMG})_2$ and $\text{Ni}(\text{EMG})_2$. The solid state and chloroform solution infrared spectra of $\text{Ni}(\text{EMG})_2$ were measured by Caton (28). He concluded that the hydrogen bond system did not undergo a large rearrangement upon dissolution of $\text{Ni}(\text{EMG})_2$ into chloroform as judged by only a small shift in the OH stretching frequency.

2. Apparatus and procedures

A Beckman IR-7 spectrophotometer was used to obtain the infrared spectra.

The halocarbon oil mulls were prepared by mixing the finely ground chelates with the halocarbon oil. The dry chelates were ground extra long in an agate mortar and pestle before mulling.

Attempts to obtain chloroform solution infrared spectra of the chelates failed to produce any OH bands due to the low solubility of the chelates.

Also, attempts to obtain matrix isolated infrared spectra of the chelates failed. The $\text{Ni}(\text{DMG})_2$ was vacuum sublimed from a Knudsen cell simultaneously with a stream of hexachloroethane onto a CsI window attached to a cryostat filled with a Dry Ice-acetone slush. In order to place enough chelate on the window to see the weak OH bands and yet maintain a matrix isolated chelate required a thick layer of hexachloroethane. The sample then absorbed or scattered too much light to

obtain a useful spectrum.

3. Experimental results

The infrared spectra of Ni(Niox)₂, Ni(Heptox)₂, Ni(3-MeNiox)₂, Ni(4-MeNiox)₂, and Ni(4-IsopNiox)₂ are illustrated in Figure 10. Tables 12, 13, 14, 15, and 16 list the frequencies of the band maxima. Assignments of the bands are indicated in the tables. The assignments were made by comparison to those made by Caton (28) for Ni(DMG)₂ and Ni(EMG)₂.

Table 12. Infrared halocarbon mull spectrum of Ni(Niox)₂

Wave number, cm ⁻¹	Assignment
2947 2865	CH stretching vibrations
2330	OH stretching vibration
1945	
1775	OH bending vibration
1570	CN stretching vibration
1457	CH bending vibrations
1445	
1412	
1338	
1332	
1323	

Table 13. Infrared halocarbon mull spectrum of Ni(Heptox)₂

Wave number, cm ⁻¹	Assignment
2930	CH stretching vibrations
2855	
2702	
2682	
2672	
2323	OH stretching vibration
2177	OH bending vibration
1790	
1563	
1456	CH bending vibrations
1447	
1437	
1355	
1344	
1340	
1333	

Table 14. Infrared halocarbon mull spectrum of Ni(3-MeNiox)₂

Wave number, cm ⁻¹	Assignment
2958	CH stretching vibrations
2932	
2873	
2857	
2320	OH stretching vibration
2180	OH bending vibration
1780	
1568	
1455	CH bending vibrations
1429	
1376	
1336	

Table 15. Infrared halocarbon mull spectrum of Ni(4-MeNiox)₂

Wave number, cm ⁻¹	Assignment
2956	CH stretching vibrations
2932	
2878	
2855	
2328	OH stretching vibration
2186	
1781	OH bending vibration
1570	CN stretching vibration
1454	CH bending vibrations
1414	
1375	
1335	

Table 16. Infrared halocarbon mull spectrum of Ni(4-IsopNiox)₂

Wave number, cm ⁻¹	Assignment
2965	CH stretching vibrations
2938	
2876	
2322	OH stretching vibration
2185	
1783	OH bending vibration
1572	CN stretching vibration
1468	CH bending vibrations
1444	
1413	
1388	
1368	
1338	

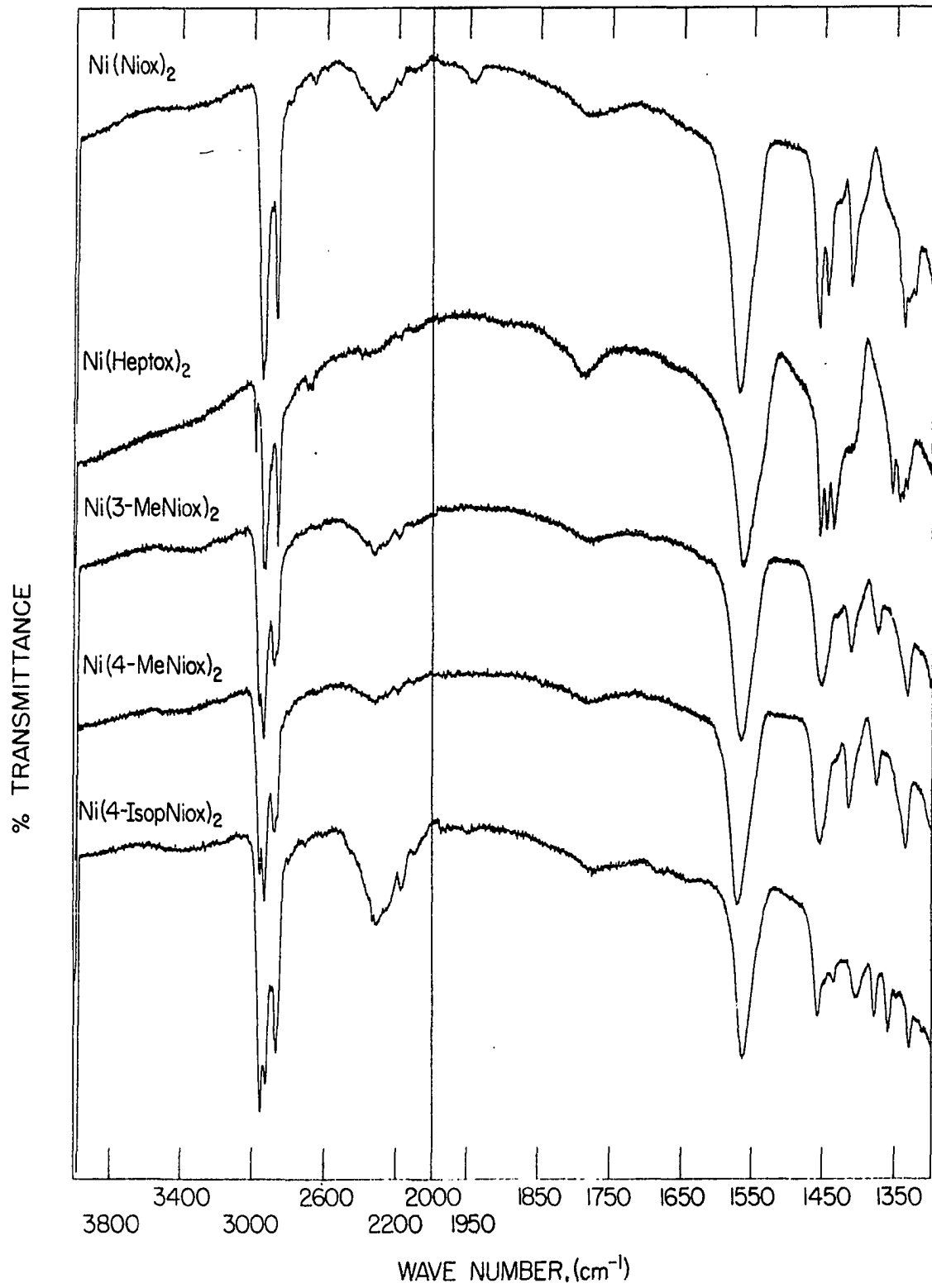


Figure 10. Infrared spectra of some Ni(II)-vic-dioximes

E. Differential Thermal Analysis of Some Metal-vic-Dioximes

1. General considerations

Several of the metal-vic-dioximes were studied by differential thermal analysis, DTA. DTA is a thermal technique in which the heat effects, associated with physical and chemical changes, are recorded as a function of temperature or time as the substance is heated at a uniform rate. Heat or enthalpic changes, either exothermic or endothermic, are caused by phase transitions or chemical reactions. Generally speaking, phase transitions, dehydration, reduction, and some decomposition reactions produce endothermic effects, whereas crystallization, oxidation, and some decomposition reactions produce exothermic effects (84).

In DTA the sample temperature is continuously compared with a reference material temperature, the difference in temperature, ΔT , being recorded as a function furnace temperature. The reference material is a thermally inert substance having a similar heat capacity as the sample. α -Alumina and glass beads are common reference materials. The sample and the reference material are placed in the heating block containing two symmetrically located and identical chambers. Identical thermocouples are placed in each, and the temperature difference is recorded as the block is heated. The temperature of the block is monitored by a third thermocouple placed in a third chamber containing reference material.

DTA is a well-established technique, and the reader is referred to the literature for further details. The works of Wendtland (84) and Smothers and Chiang (77) are recommended.

Many of the metal-vic-dioximes have been long known to decompose at temperatures of about 250°C (78). The DTA study was undertaken to determine if any phase changes or reactions were occurring before the decomposition point. The thermal character of the decomposition of the chelates should be revealed from the study. The DTA curves should show how the character of the chelate affects its thermal stability.

2. Apparatus and procedures

A DuPont 900 Differential Thermal Analyzer was used for the DTA study. The sample and the reference material, glass beads, were put in 2-mm diameter glass melting-point capillary tubes and placed in the holes provided in the heating block. Thermocouples were inserted into the sample and reference tubes through the top of the open glass tubes. A glass bell jar, seated on a Neoprene O-ring, was placed over the entire sample and furnace assembly. The bell jar was evacuated and then filled with either argon or nitrogen. The evacuation and filling step was repeated three times. A stream of inert gas was then passed through the jar at a rate of 2 ft³/hr. The heating block was heated at a rate of 20°C/min.

3. Experimental results

The DTA curves for Ni(DMG)₂ and Ni(EMG)₂ are shown in

Figure 11. The DTA curves of the other chelates studied had the same shape as that of Ni(DMG)₂. Each exhibited a slight exothermic rise just before decomposition and then a large exothermic loop upon decomposing. The evolution of smoke and bubbling in the sample tube has observed at the decomposition point for the chelates. The decomposition points found for the metal-vic-dioximes studied are listed in Table 17. The decomposition point for each chelate was found by extending the baseline and the straight portion of the exotherm to the point where they cross as shown in Figure 11 for Ni(DMG)₂.

Duplicate runs on several of the chelates showed the technique to be highly reproducible.

Table 17. Decomposition points of some metal-vic-dioximes as determined by differential thermal analysis

Chelate	Decomposition temperature, °C
Ni(DMG) ₂	321
Ni(Niox) ₂	293
Ni(Heptox) ₂	294
Ni(3-MeNiox) ₂	270
Ni(4-MeNiox) ₂	284
Ni(4-IsopNiox) ₂	272
Ni(EMG) ₂	275
Pd(DMG) ₂	342
Pt(DMG) ₂	315

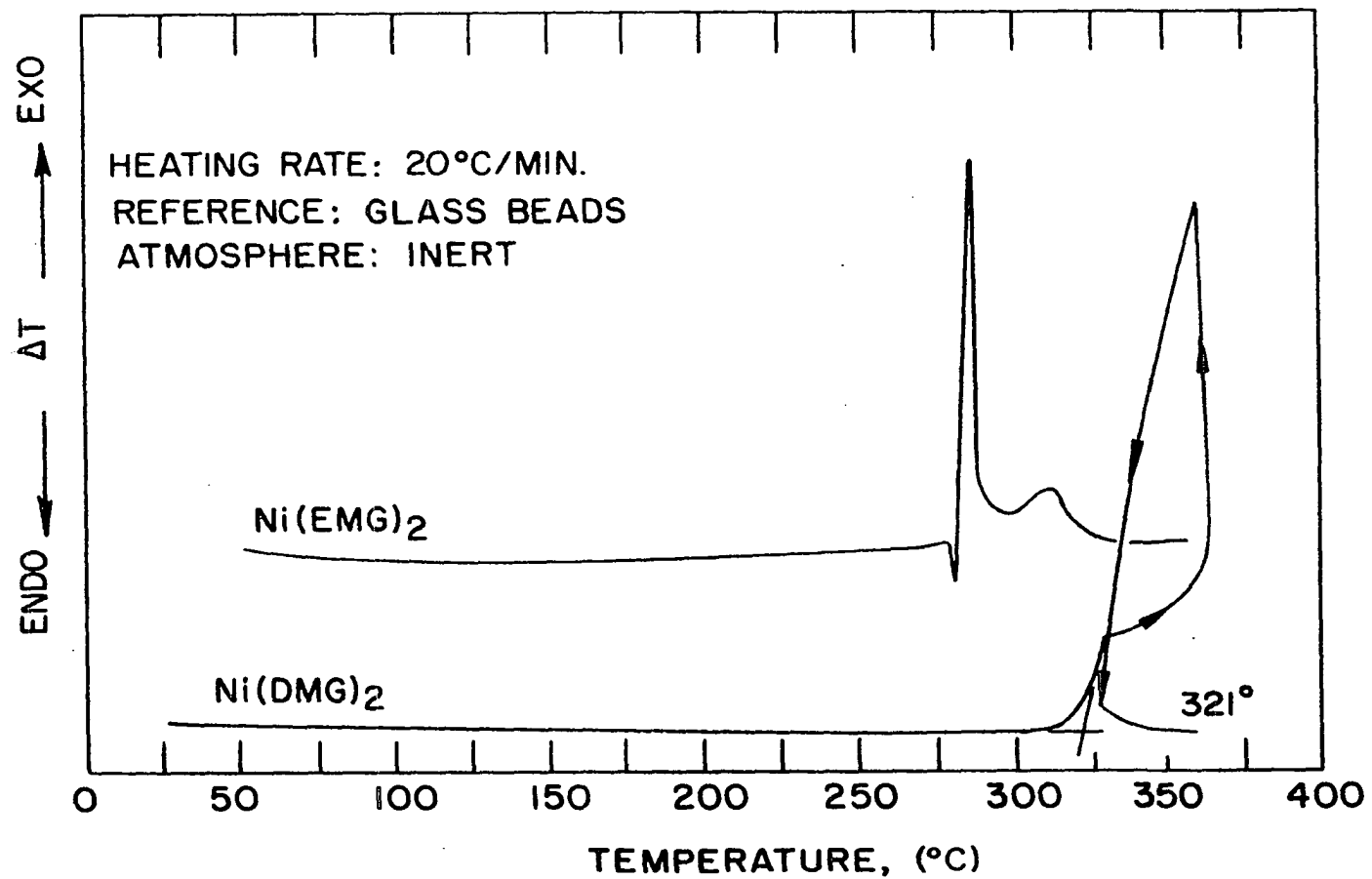


Figure 11. Differential thermal analysis curves for Ni(DMG)₂ and Ni(EMG)₂

V. DISCUSSION AND CONCLUSIONS

A. Solubility Studies

1. Solubility in chloroform

The solubilities of the Ni(II)-vic-dioximes in chloroform at 25°C are listed in Table 6. The values reported by Hooker (51) are noted to be higher than those found in this work.

The solubility of the chelates is noted to be highly dependent on the character of the ligand. Ni(Niox)₂ is found to be two orders of magnitude less soluble in chloroform than Ni(Heptox)₂ and the substituted nioxime chelates of nickel. Ni(DMG)₂ has a solubility value intermediate to those of Ni(Niox)₂ and Ni(Heptox)₂. Evidently the substituent on the nioxime ring is able to interact with the solvent to a much greater extent than the nioxime itself. This is probably not to be unexpected since the substituent would increase the area of the molecule with a resultant increase in van der Waals type interactions between the chelate and the chloroform being possible.

2. Solubility in n-heptane

The solubilities of the Ni(II)-vic-dioximes in n-heptane at 25°C are tabulated in Table 7. The solubility values are noted to be in the same order as those found in chloroform; that is, Ni(Heptox)₂ and the substituted nioxime chelates are an order of magnitude more soluble than Ni(DMG)₂ which is

about an order of magnitude more soluble than $\text{Ni}(\text{Niox})_2$.

No correlation between the solubilities of the $\text{Ni}(\text{II})$ -vic-dioximes in n-heptane and the Ni-Ni distance in the solid chelates was found. Note that $\text{Ni}(\text{DMG})_2$, $\text{Ni}(\text{Niox})_2$, and $\text{Ni}(4\text{-MeNiox})_2$ have essentially the same Ni-Ni distance in their crystalline state.

The solubilities of the chelates in n-heptane appear to be influenced mostly by the character of the ligand rather than their Ni-Ni distances in the crystalline state.

B. Thermodynamic Studies

1. Dissolution of $\text{Ni}(\text{II})$ -vic-dioximes in n-heptane

The thermodynamic data for the dissolution of the $\text{Ni}(\text{II})$ -vic-dioximes in n-heptane are tabulated in Table 9.

The solubility value, $-\log X_2$, of $\text{Ni}(\text{EMG})_2$ in n-heptane at 25°C was found to be 5.25, whereas Anderson (3) reported a value of 6.74. Anderson used a double extraction procedure to determine the solubility values for $\text{Ni}(\text{EMG})_2$ in n-heptane. It might be that some of the chelate was lost in his rather complicated procedure. The value reported here seems more reasonable when it is noted that other $\text{Ni}(\text{II})$ -vic-dioximes are a little greater than an order of magnitude more soluble in carbon tetrachloride than in n-heptane. Anderson (3) reported the solubility, i.e., $-\log X_2$, of $\text{Ni}(\text{EMG})_2$ in carbon tetrachloride at 25°C to be 4.10 using a procedure similar to that used here.

The heat of solution found for Ni(EMG)₂ in n-heptane was found to be 2.8 kcal/mole more endothermic than that found by Anderson.

The solubility values and heat of solution found for Ni(DMG)₂ in n-heptane were found to agree within experimental error with those of Fleischer (40).

The Ni-Ni distances in the crystalline state, the heats of solution, and the free energies for the Ni(II)-vic-dioximes are tabulated together in Table 18.

Table 18. Ni-Ni distances, heats of solution, and free energies for some Ni(II)-vic-dioximes^{a, b}

Chelate	Ni-Ni distance (Å)	ΔH° (kcal/mole)	ΔG° (kcal/mole)
Ni(4-IsopNiox) ₂	3.19	9.5	8.96
Ni(DMG) ₂	3.233	14.1	10.17
Ni(Niox) ₂	3.237	13.4	11.45
Ni(4-MeNiox) ₂	3.24	12.6	9.22
Ni(3-MeNiox) ₂	3.47	9.3	8.38
Ni(Heptox) ₂	3.596	13.6	9.13
Ni(EMG) ₂	4.75 ^c	8.6	6.56

^aStructure data are taken from Table 3, and the thermodynamic data for dissolution in n-heptane are taken from Table 9.

^bStandard state taken as mole fraction one and 298.16°K.

^cNi(EMG)₂ has a different crystal structure than the other members of the series.

Two points can be made from the data in Table 18.

1) There is no apparent relationship between the heats of solution and the Ni-Ni distance in the crystals of the Ni(II)-vic-dioximes. 2) The heat of solution for Ni(EMG)₂ is only slightly lower than the other members of the series. If the heats of solution in n-heptane are taken as a measure of the relative crystal energies of the chelates, then the conclusion of this study would have to be that any possible Ni-Ni interactions are not the important factor in stabilizing the crystals. However, it must be kept in mind that one cannot isolate completely the ligand effects from the Ni-Ni effects in this type of study.

2. Dissolution of Ni(DMG)₂, Pd(DMG)₂, and Pt(DMG)₂ in carbon tetrachloride

The thermodynamic data for the dissolution of the chelates are tabulated in Table 11. Structure data taken from Table 3 and thermodynamic data taken from Table 11 are listed together in Table 19.

Ni(DMG)₂, Pd(DMG)₂, and Pt(DMG)₂ are known to be isomorphous and to have essentially the same metal-metal distance in their crystals.

The theory Rundle (72) proposed for the explanation of the possible weak metal-metal bonding in the metal-vic-dioximes above involved the formation of molecular orbitals by combining the p_z and d_z^2 orbitals of adjacent metal atoms

Table 19. Structure and thermodynamic data for Ni(DMG)₂, Pd(DMG)₂, and Pt(DMG)₂^a

Chelate	Distances in Å		ΔH° (kcal/mole)	ΔG° (kcal/mole)
	M-M	M-N ^b		
Ni(DMG) ₂	3.233	1.85	15.3	8.50
Pd(DMG) ₂	3.255	1.935	7.4	8.21
Pt(DMG) ₂	3.235	1.94	10.6	9.28

^aStandard state taken as mole fraction one and 298.16°K.

^bMean values.

along the metal atom chains in the crystalline state. The molecular orbitals formed by the combination of these orbitals supposedly then interact with a resulting net weak bonding in the system by configuration interaction as was discussed in the LITERATURE REVIEW. In comparing the possibilities for bonding in Ni(DMG)₂, Pd(DMG)₂, and Pt(DMG)₂ by this scheme, it would seem that the palladium and platinum complexes would have more overlap than Ni(DMG)₂ since their outer orbitals are 4d and 5d, respectively. The larger spatial extension of the larger orbitals should allow more interaction over the 3.24Å^o intermetallic distance. Thus, if there is a bonding interaction of the molecular orbitals, the palladium and platinum interactions should be larger than that of the nickel interaction in these chelates.

It is interesting to note that the conductivities along the metal chain for [Pt(NH₃)₄]²⁺[PtCl₄]²⁻ is on the order of

10^6 times greater than that of $[\text{Pt}(\text{NH}_3)_4]^{2+}[\text{PdCl}_4]^{2-}$ (75).

This would be consistent with the above hypothesis but does not necessarily say anything about the interaction being bonding.

The thermodynamic data for $\text{Ni}(\text{DMG})_2$, $\text{Pd}(\text{DMG})_2$, and $\text{Pt}(\text{DMG})_2$ do not support the hypothesis of any significant metal-metal bonding in the crystals of these chelates. If one assumes that the heats of solution are a measure of the relative crystal energies, the $\text{Ni}(\text{DMG})_2$ is found to be the most stable. This is the reverse of the expected result if metal-metal bonding were the important feature in stabilizing these chelates. Evidently, other factors, such as, packing and electrostatic considerations, are the dominant features in determining the crystal energies of these chelates. From this viewpoint, the smaller nickel chelate would be expected to be the more stable. This was the observed fact. Other workers (4,14,60) have reached this conclusion in considering the stabilities of similar chelates.

C. Spectral Studies

1. Visible and ultraviolet spectra

The gas phase and chloroform solution spectra for $\text{Ni}(\text{DMG})_2$ and $\text{Ni}(\text{EMG})_2$ are shown in Figure 8 and 9, respectively. The gas phase and chloroform solution spectra were found to be nearly identical in both cases. Thus, the color band is a phenomenon of the solid state, and it can be said

with certainty that no unusual solvation effects are altering the chloroform solution visible and ultraviolet spectra.

2. Infrared spectra

The frequencies of the stretching and bending vibrations for the series of Ni(II)-vic-dioximes are tabulated in Table 20. Illustrations of the spectra taken in this study are shown in Figure 10.

Table 20. Frequency of OH bands of some Ni(II)-vic-dioximes

Chelate	OHO distance in Å	ν_{OH}^a	δ_{OH}^b
Ni(EMG) ₂	2.33	2388 ^c	1784 ^c
Ni(EMG) ₂		2350 ^{c,d}	1715 ^{c,d}
Ni(DMG) ₂	2.40	2322 ^c	1790 ^c
Ni(Niox) ₂	---- ^e	2330	1775
Ni(Heptox) ₂	---- ^e	2323	1790
Ni(3-MeNiox) ₂	---- ^e	2320	1780
Ni(4-MeNiox) ₂	---- ^e	2328	1781
Ni(4-IsopNiox) ₂	---- ^e	2322	1783

^a ν is stretching vibration in cm^{-1} .

^b δ is bending vibration in cm^{-1} .

^c Values taken from Caton (28).

^d Chloroform solution spectrum.

^e O-H-O distance has not been determined.

The OH bands in the spectra were all noted to be very similar in both shape and frequency. This implies the hydrogen bond systems of all chelates in this series are nearly identical.

It was noted earlier that Caton (28) concluded the hydrogen bond system for Ni(EMG)_2 was not altered significantly upon dissolution in chloroform. The same statement should hold for the dissolution of the other chelates in chloroform and especially for dissolution in n-heptane and carbon tetrachloride. The latter two solvents would have no tendency to hydrogen bond with the chelates. Unfortunately, the low solubility of these chelates, except that of Ni(ENG)_2 in chloroform, prohibited a test of this assumption.

However, it seems safe to say that no rearrangement of the hydrogen bond system is occurring upon the solution of the $\text{Ni(II)-vic-dioximes}$. Therefore, the comparison of the heats of solution for the series in n-heptane should be valid as no unusual energy contributions to the enthalpy term for any one member of the series is occurring due to molecular rearrangements. The chelates can thus be treated as organic type solutes.

Drugov (34) assigned the OH stretching frequencies for some $\text{Ni(II)-vic-dioximes}$. The values he assigned for Ni(Niox)_2 and Ni(Heptox)_2 (1775 cm^{-1} for each) are in agreement with the frequencies assigned in this work for the OH

bending vibrations. The OH stretching frequencies are now known to be in the 2300 cm^{-1} region (18,28). No attempt has been made here to predict actual O---O distances in the chelates. It has been shown that the OH stretching frequency shift with change in O---O distance goes through a maximum (57,28). There are not enough x-ray data presently available for very short O-H-O distances to make accurate predictions of their distances from their stretching frequencies.

However, it is reasonable to assume that the Ni(II)-vic-dioximes in the above series have O---O distances very close to that of Ni(DMG)₂.

D. Differential Thermal Analysis Study

The DTA curves for Ni(DMG)₂ and Ni(EMG)₂ are shown in Figure 11. The decomposition points found for the chelates studied are given in Table 17. No endotherms or exotherms were found for any of the pure chelates before the decomposition point. An endotherm was noted at about 195°C for some crude Ni(EMG)₂. This peak did not appear in the DTA curve of the chelate after the Ni(EMG)₂ was purified either by recrystallization or vacuum sublimation.

Ni(EMG)₂ and the substituted nioxime chelates of nickel were noted to decompose at lower temperatures than the other chelates studied. The dimethylglyoxime chelates were noted to be the most thermally stable.

VI. SUMMARY

Solubility and thermodynamic values for the dissolution of some metal-vic-dioximes in various solvents have been determined. The data do not support the hypothesis of weak metal-metal bonding as being the important factor in stabilizing the crystals where metal-metal chains are found. The solubility behavior of the Ni-, Pd-, and Pt-vic-dioximes can be explained on the basis of packing and electrostatic considerations. This conclusion is consistent with recent studies by other researchers.

The difference in the heat of solution between the Ni(II)-vic-dioximes with metal-metal chains and that of Ni(EMG)₂ was found not to be as large as that found by Anderson (3).

The metal-metal bonding hypothesis for the metal-vic-dioximes of nickel, palladium, and platinum has provided a framework for a systematic study of these chelates. It has been very successful in rationalizing the unique behavior of these chelates, and much of the early research tended to substantiate the hypothesis. Indeed, there are metal-metal interactions in the crystalline state of these chelates, but in view of the recent spectroscopic studies of Anex and Krist (4) and others (14,28), there is strong doubt as to whether these interactions are bonding in character. The thermodynamic data presented here tend to support this view.

Considering the data presented here in light of all the

other evidence, it appears that the low solubility of the Ni(II)-, Pd(II)-, and Pt(II)-vic-dioximes is due to the formation of very stable square planar chelates which form stable crystals which have little tendency to be solvated by common solvents. Metal-metal interactions resulting from the nature of the crystal packing give rise to unique optical properties. These metal-metal interactions do not seem to be important in stabilizing these crystals.

The gas phase spectra of Ni(DMG)₂ and Ni(EMG)₂ were found to be nearly the same as the chloroform solution spectra. This verifies the assumption made by other workers (10,4,14) that this is the case.

Infrared spectra of some Ni(II)-vic-dioximes in the 4000 to 1300 cm⁻¹ region were taken. Assignments for the OH stretching and bending vibrations were made. It is predicted that the O---O distances in these chelates are very close to that found in Ni(DMG)₂.

A differential thermal analysis study of some metal-vic-dioximes showed that the chelates decompose exothermally. No phase changes were noted for any of the chelates before the decomposition point.

VII. SUGGESTIONS FOR FUTURE WORK

1. Anisotropic electrical conductivity measurements should be made on $\text{Ni}(\text{DMG})_2$, $\text{Pd}(\text{DMG})_2$, and $\text{Pt}(\text{DMG})_2$ in view of recent findings for Magnus green type complexes (68,75, 17). If it is found that $\text{Pt}(\text{DMG})_2$ has the properties of a semiconductor, it may be that it would be possible to synthesize intermetallic polymers with vic-dioxime coordination sites which would be semiconducting.

2. The O---O distances in more of the $\text{Ni}(\text{II})$ -vic-dioximes should be measured. This information would be useful in establishing a relationship between the O---O distance and the frequency of the OH stretching vibrations for short hydrogen bond systems.

3. Measurement of the magnetic susceptibility dependence on temperature for $\text{Ni}(\text{DMG})_2$, $\text{Pd}(\text{DMG})_2$, and $\text{Pt}(\text{DMG})_2$ should be considered. In a preliminary study the magnetic susceptibility of $\text{Ni}(\text{DMG})_2$ at 24° , 93° , and 153°C was measured. No change in the magnetic susceptibility was noted over the temperature range, and a value of $\chi_M = -110 \times 10^{-6}$ emu/mole was found. This is in close agreement with Banks, et al. ($\chi_M = -108 \times 10^{-6}$ emu/mole) (12). This means that the separation between the first excited state and the ground state is 1000 - 3000 cm^{-1} or greater (about 3 - 9 kcal/mole). Similar experiments for $\text{Pd}(\text{DMG})_2$ and $\text{Pt}(\text{DMG})_2$ might show that they have lower Néel temperatures than $\text{Ni}(\text{DMG})_2$. This study

might shed some light on the electronic structure of the metal atoms in these chelates.

4. The assumption has been made that the difference in the heats of solvation for the metal-vic-dioximes is negligible in inert solvents, such as, n-heptane and carbon tetrachloride. To be completely rigorous, this assumption should be tested by determining the heats of sublimation of these chelates. A preliminary experiment was performed in which the chelates were heated in a vacuum oven at pressures of about 10 Torr. Many of the chelates showed signs of decomposition before significant weight loss by sublimation was noted. However, if a higher vacuum were used, it might be possible to make the necessary measurements. The work of Wood and Jones should be noted (87).

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