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Metal-metal bonds and physical properties of some nickel (II)-vic-dioxime complexes

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METAL-METAL BONDS AND PHYSICAL PROPERTIES
OF SOME NICKEL(II)-VIC-DIOXIME COMPLEXES

by

Samuel Anderson

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

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Of Science and Technology
Ames, Iowa

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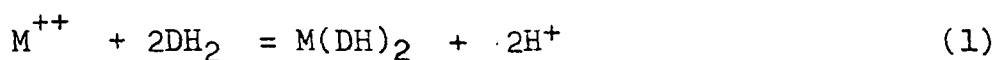
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INTRODUCTION

Purpose of Research

The vic-dioxime group is one of the most highly selective of the organic analytical reagents. It precipitates nickel(II) from weakly acid, neutral, or slightly alkaline solutions, and palladium(II) from moderately acid solutions (46) according to equation 1,



where M^{++} represents a metal ion and DH_2 represents a vic-dioxime. The characteristics of the vic-dioxime group were discovered by Tschugaeff in 1905 (46). The vic-dioximes have been used extensively as reagents for nickel(II) since Brunck (12, 13, 14) originally proposed that 2,3-butanedionedioxime (dimethylglyoxime) be used for the gravimetric determination of nickel(II).

In their work on the crystal structure of nickel dimethylglyoxime, Godycki and Rundle (26) proposed that the nickel atoms in the crystal are close enough to participate in metal-metal bonding. They also proposed that this metal-metal bonding may be the reason for the high selectivity of the vic-dioxime group for nickel(II). With this view in mind, Banks and Barnum (4) made a study of the metal-metal bond distance and the solubility for several nickel(II) vic-dioximes. They were able to establish only a rough correlation. The heats of

solution of nickel(II) dimethylglyoxime and copper(II) dimethylglyoxime in various solvents were measured by Fleischer (22). His conclusion was that the nickel-nickel bond does not contribute appreciably to the lattice energy of nickel dimethylglyoxime.

The purpose of this research is to study some of the properties of the nickel(II)-vic-dioxime complexes which may lead to a better understanding of the fundamental nature of these reagents and the reason for their selectivity. A selective reagent is one which will react in a certain manner with a limited number of metals. A specific reagent is one which will give a quantitative reaction such as a color or precipitate with a desired metal ion with no interfering reactions with other metal ions which may be present. Some of the properties of the nickel(II)-vic-dioxime complexes which have been studied during the course of this work are solubility, stability and metal-metal bond distance in the crystal. The stability constants of the nickel(II)-vic-dioxime complexes were determined in dioxane-water solution and extrapolated to water solution. Because these nickel(II)-vic-dioxime complexes are so insoluble in aqueous solutions, it becomes expedient to determine their stability in mixtures of water and organic solvent. Charles and Freiser (18) have measured the stability constant of the nickel(II) complex of dimethylglyoxime in 50% (v/v) dioxane-water mixture. The

solubility products have been determined in water; the heats of solution of some of the reagents in water have been compared. A study has been made to find out if there are other nickel(II)-vic-dioxime complexes, other than those studied by Banks and Barnum (4), which have nickel atoms close enough in the crystal to participate in metal-metal bonding.

Nomenclature and Notation

The systematic names of the vic-dioximes are those proposed by the International Union of Chemistry (35). The trivial names of the vic-dioximes and their complexes will be used in this thesis. The trivial names and the systematic names of most of the compounds used are listed in Table 1. The notations used are given in Table 2.

Table 1. Nomenclature of compounds used in this research

Systematic name	Trivial name
2,3-butanedionedioxime	dimethylglyoxime
2,3-pentanedionedioxime	ethylmethylglyoxime
3,4-hexanedionedioxime	diethylglyoxime
4,5-octanedionedioxime	dipropylglyoxime
1,2-cyclohexanedionedioxime	nioxime
3-methyl-1,2-cyclohexanedionedioxime	3-methylnioxime

Table 1. (Continued)

Systematic name	Trivial name
4-methyl-1,2-cyclohexanedionedioxime	4-methylnioxime
1,2-cycloheptanedionedioxime	heptoxime
bis(2,3-butanedionedioximato- <u>N,N'</u>) nickel(II)	nickel dimethylglyoxime
bis(2,3-pentanedionedioximato- <u>N,N'</u>) nickel(II)	nickel ethylmethylglyoxime
bis(3,4-hexanedionedioximato- <u>N,N'</u>) nickel(II)	nickel diethylglyoxime
bis(4,5-octanedionedioximato- <u>N,N'</u>) nickel(II)	nickel dipropylglyoxime
bis(1,2-cyclohexanedionedioximato- <u>N,N'</u>) nickel(II)	nickel nioxime
bis(1,2-cycloheptanedionedioximato- <u>N,N'</u>) nickel(II)	nickel heptoxime
bis(3-methyl-1,2-cyclohexanedionedioximato- <u>N,N'</u>) nickel(II)	nickel 3-methylnioxime
bis(4-methyl-1,2-cyclohexanedionedioximato- <u>N,N'</u>) nickel(II)	nickel 4-methylnioxime

Table 2. Notations used in this thesis

Symbol	Meaning of symbol
A	Absorbancy or a constant in the Debye-Hückel equation.
A. U.	Angstrom units.

Table 2. (Continued)

Symbol	Meaning of symbol
a_i	Activity of species <u>i</u> .
DH_2	A <u>vic</u> -dioxime.
DH^-	The anion of a <u>vic</u> -dioxime.
f_i	The activity coefficient of a species <u>i</u> .
K_a	The acid dissociation constant of a ligand in water solution.
\bar{K}_a	The acid dissociation constant of a ligand in dioxane-water solution.
\bar{K}_1	Over-all stability constant for a one to one complex in dioxane-water solution.
K_1	Over-all stability constant for a one to one complex in water.
\bar{K}_2	Over-all stability constant in dioxane-water solution for a complex with ligand to metal ratio of 2:1.
K_2	Same as preceding symbol except that the solution is water.
K_{sp}	Solubility product constant.
K_s	Intrinsic solubility constant.
M^{++}	A divalent metal ion.
$m\mu$	Wavelength of light expressed in millimicrons.
\bar{n}	Formation function of Bjerrum.
pK	Negative logarithm of a constant.
S	Solubility expressed in moles per liter.
ϵ	Molar absorptivity, liter/mole-cm.

Table 2. (Continued)

Symbol	Meaning of symbol
λ	Wavelength of light.
μ	Ionic strength.

Other notations which are used will be explained at the time of use if they are not obvious.

REVIEW OF THE LITERATURE

Structure of vic-Dioxime Complexes

The reaction of the vic-dioxime with metal(II) ions was first reported in 1905 by Tschugaeff (46). He showed that the vic-dioximes react with nickel(II) to give a 2:1 complex and that two moles of hydrogen are liberated in the reaction. The incorrect assignment of the isomeric forms of the vic-dioximes caused confusion for a while in the structure assigned to the nickel complex. The vic-dioximes may exist in three isomeric forms, syn, amphi, and anti. Of the three stereoisomers, only the anti-isomer is capable of forming the characteristic red, insoluble complex with nickel (34). The anti-form was mistakenly assigned the syn-configuration on the basis of the Beckmann Rearrangement, assuming the groups which interchanged in the rearrangement were the cis-groups. Meisenheimer (34) showed, however, that the trans-groups are interchanged in the Beckmann Rearrangement.

The amphi-dioximes give yellow or green-yellow compounds with nickel in which one molecule of dioxime is attached to one atom of nickel, the hydrogens of both oxime groups being replaced. The metal is attached to one group through nitrogen and the other through oxygen. The syn-dioximes are completely incapable of forming compounds with the metals.

Because the anti-dioxime is the only one which forms a stable complex with metals, all other forms tend to be

converted to that form in acid solution.

Pfeiffer (38) showed that the coordination occurs through the nitrogen while Brady and Muers (11) suggested that hydrogen bonding occurs between neighboring oxygen atoms. They found that nickel dimethylglyoxime gives no methane with methyl magnesium iodide in amyl ether.

The hydrogen bonded structure of the nickel(II) vic-dioxime complexes was shown to exist in a square planar configuration by Sugden (44). The diamagnetic properties of these complexes were investigated by several workers (6, 17, 32) and according to Pauling (36) must contain dsp^2 square planar bonds.

The nature of the hydrogen bonding in several nickel(II) vic-dioxime complexes has been investigated by Godycki, et al. (27) and Voter, et al. (50). They also studied the deuterated complexes. The infrared absorption spectra of the nickel(II) complexes of the vic-dioximes reveal that the characteristic absorption maxima normally attributed to O--H bonds are not detected in the usual region. These maxima, shifted to lower frequencies, are noted in the spectra of the corresponding solid vic-dioximes. The conclusion is drawn that the oxime hydrogens of the nickel(II) derivatives are present in an O--H--O structure unlike that observed in normal hydrogen bonds. After observing only one absorption band for the N--O group, Rundle and Parasol (42) concluded that the hydrogen

bonds were symmetrical. Two such bands would be observed if the hydrogen bonds were not symmetrical. However, later work by Blinc and Hadzi (9) indicated that the hydrogen bonds may not be symmetrical and that the proton does not occupy a central position between two oxygen atoms.

The crystal structure of nickel dimethylglyoxime was determined by Godycki and Rundle (26). They found that the complex is square planar and the nickel atoms lie in a straight row which extends throughout the length of the crystal. Furthermore, the distance between two adjacent nickel atoms is believed to be short enough to allow metal-metal bonding.

Godycki and Rundle (26) suggested that the selectivity of dimethylglyoxime is due to the metal-metal bonds which contribute stability to the crystal. With this view in mind, Banks and Barnum (4) made a study of the metal-metal bond length and the solubility product constant of several vic-dioxime complexes. They were able to establish only a rough correlation.

Banks and Barnum (5) observed that colloidal suspensions of the nickel vic-dioximes reveal a new absorption band in the visible region of the spectrum which is not present when the complex is dissolved in organic solvents. They suggested that this new band was due to metal-metal bonding in the solid state.

Dyrssen and Hennichs (20) studied the solubility of nickel dimethylglyoxime and copper dimethylglyoxime and concluded that the large difference in solubility between the two complexes in water is due to the fact that copper has a tendency to be five coordinated while nickel has only the coordination number of four in their respective complexes with dimethylglyoxime.

Frasson, et al. (23) determined the crystal structure of copper dimethylglyoxime. They found that copper does exhibit a coordination number of five by bonding with an oxygen in an overlying molecule.

Fleischer (22) determined the heat of solution of copper dimethylglyoxime in several solvents from the temperature dependence of their solubility. He found that the crystal of copper dimethylglyoxime is more stable than the crystal of nickel dimethylglyoxime by 2 or 3 kcal. Therefore, he concludes that if nickel-nickel bonds exist in nickel dimethylglyoxime, they must be very weak.

Stability Constants and Solubility Product Constants

The low solubility of the nickel(II)-vic-dioxime complexes in water makes it desirable to use mixtures of water and organic solvents to determine their stability. Calvin and Wilson (16) employed the glass electrode in 50% aqueous-dioxane mixtures for pH measurements in order to determine the stability of metal-ligand complexes of low solubility.

Charles and Freiser (18) have measured the stability constants of nickel(II) complexes of dimethylglyoxime and its monomethylether in 50% (v/v) aqueous-dioxane. They found that the nickel(II)-dimethylglyoxime complex is more stable than the corresponding complex with the monomethyl ether. Because hydrogen bonding can not take place in the monomethyl ether, this is just what is to be expected. Furthermore, the copper(II)-dimethylglyoxime complex is more stable than the corresponding nickel(II) complex. Thus, the selectivity of dimethylglyoxime as a precipitant for nickel(II) must be due to some factor, or factors other than stability, perhaps solubility.

Christopherson and Sandell (19) have determined the stability constant of nickel(II)-dimethylglyoxime in aqueous solution using pH measurements and solubility data.

Bochkova and Peshkova (10) have determined the stability constant of the nickel(II), copper(II) and cobalt(II) complexes of dimethylglyoxime in 50% (v/v) aqueous-dioxane mixtures.

Van Uitert and Fernelius (48) determined the stability constant for the nickel(II) dimethylglyoxime complex in 75% dioxane-25% water (v/v) at 30°.

In order to use pH measurements to determine the formation function of a metal-ligand complex, it is necessary that the acid dissociation constant of the ligand be known. Banks and Carlson (6) have determined the acid dissociation

constants of several vic-dioximes in water solution. Several other workers (2, 3, 4, 19, 52) also have determined the acid dissociation constants of several vic-dioximes in water solution.

Several workers (2, 10, 18, 48) have determined the acid dissociation constant of dimethylglyoxime in aqueous mixtures of dioxane.

The relationship between the stability of metal-ligand complexes in water solution and in mixtures of water and organic solvents has been investigated by Irving and Rossotti (30). If the metal-ligand complex is sufficiently soluble in water, the stability may be measured in various concentrations of mixed solvents and the resulting curve of stability constant against organic solvent content extrapolated to zero concentration of organic solvent. Because the nickel(II)-vic-dioxime complexes are only slightly soluble in water, the curve of stability constant versus percentage dioxane can not be accurately extrapolated to zero per cent dioxane.

APPARATUS AND REAGENTS

Reagents

Vic-Dioximes

Dimethylglyoxime was obtained from the Matheson Co. The "purified" product was recrystallized four times from a water-alcohol mixture.

Nioxime was prepared using the procedure of Rauh, et al. (39), Geissman and Schlatter (26), and Hach, Banks and Diehl (28). Heptoxime was prepared by the method of Vander Haar, Voter and Banks (47). Each was recrystallized at least three times from a water-alcohol mixture before use.

3-Methylnioxime and 4-methylnioxime were prepared in this laboratory by the procedures described by Banks, Hooker, and Richard (7).

Diethylglyoxime and dipropylglyoxime were prepared by the procedures of Snell and McElvain (43), Wegmann and Dahn (51), and Bryant and Smith (15).

Methylethylglyoxime was prepared by oximation of the Eastman product, 2,3-pentanedione. The procedure is described by Bryant and Smith (15).

Miscellaneous reagents

The solution of standard nickel(II) was prepared by dissolving Mond nickel in aqua-regia. An excess of perchloric acid was evaporated to near dryness to remove chloride,

nitrate and the excess perchloric acid. The nickel(II) perchlorate solution was standardized by precipitation with dimethylglyoxime.

The sodium perchlorate used for controlling the ionic strength was the "reagent-grade" product of the G. Frederick Smith Chemical Co.

Sodium hydroxide solutions were prepared from Fisher Scientific Co. "certified" reagent-grade pellets and were standardized against primary standard potassium acid phthalate.

The dioxane was purified by using the method described by Vogel (49).

All organic solvents were of "reagent-grade" quality.

Nickel(II)-vic-dioxime complexes

Nickel diethylglyoxime, nickel dipropylglyoxime, and nickel ethylmethylglyoxime were prepared in the following manner: A weighed quantity of the purified dioxime was dissolved in methanol. Water was then added until the dioxime began to precipitate and then additional alcohol was added to keep the dioxime in solution. A few drops of ammonium hydroxide was added to bring the pH to about 6 or 7 and then an excess of nickel ions was added. The precipitate was allowed to stand for about twenty four hours and then washed and filtered. The precipitate was allowed to dry in the air and then placed in an oven at 100° for one hour.

Crystals of the nickel(II)-vic-dioxime complexes were prepared by slowly recrystallizing from organic solvents. Nickel diethylglyoxime and nickel dipropylglyoxime crystals were obtained from trichloroethylene (Mallinckrodt-Transistar Grade). Crystals of nickel ethylmethylglyoxime were obtained from 1,2-dichlorobenzene (Eastman "white label" 99+%).

Apparatus

For the measurement of all absorption spectra, a Cary Model 14 recording spectrophotometer was used. Absorbancy measurements and molar absorptivities at a particular wavelength were made with a Beckman DU spectrophotometer equipped with a photomultiplier attachment.

The pH measurements were made with a Beckman Model G pH meter. All work was performed at a thermostatically controlled room temperature of 25°. The pH meter was standardized with Beckman standard buffer solution (pH 7.00 \pm 0.02) and with buffer solutions (pH 4.01 \pm 0.02, pH 9.18 \pm 0.02) prepared from Beckman buffer powders.

Rapid mixing was achieved by means of a magnetic stirrer which was stopped during actual pH measurements.

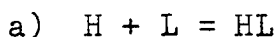
Calculations of stability constants were made with the aid of an IBM 650 electronic digital computer. The programming system used was a floating decimal interpretive system (53).

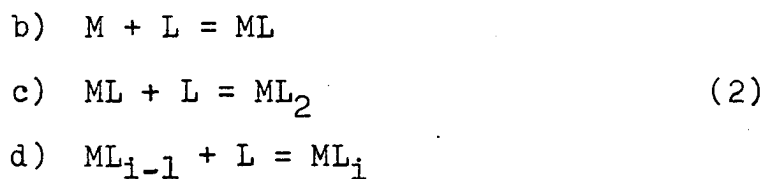
EXPERIMENTAL INVESTIGATION

The Determination of the Stability Constants of
Bis(vic-dioximato-N,N')nickel(II) ComplexesTheory

The evaluation of the stability constants of metal-ligand complexes is a useful way in which to characterize an organic ligand. Calvin and Wilson (16) obtained a quantitative evaluation of metal-ligand stability by modifying the method used by Bjerrum (8) to study the formation constants of metal amines. Peshkova (37) considered the pH of precipitation of the nickel(II) vic-dioximes as an indication of their relative stability. The pH of precipitation is related to stability but as it also involves solubility phenomena, it is not a reliable basis for the evaluation of stability. Numerous approaches have been used to determine the stability constants of metal complexes. The success with which a particular method may be used is a function of the system. The various approaches which have been used are summarized by Martell and Calvin (33), Sullivan and Hindman (45) and Rossotti and Rossotti (41).

The equilibria between the metal ion, M, in solution and a ligand, L, which form complexes may be described by the following reactions:





The stability constants may be expressed by

$$k_1 = (ML)/(M)(L) \quad (3)$$

$$k_2 = (ML_2)/(ML)(L) \quad (4)$$

$$k_i = (ML_i)/(ML_{i-1})(L) \quad (5)$$

$$K_i = k_1 k_2 k_3 \dots k_i = (ML_i)/(M)(L)^i \quad (6)$$

$$K_a = (H)(L)/(HL) \quad (7)$$

The constants have the following significance: K_i is the over all stability constant for the i -th complex and K_a is the acid dissociation constant for the ligand. The charges on the ions have been omitted for simplicity.

The analytical concentrations of the metal and the ligand may be expressed as follows:

$$(M)_T = (M) + \sum_{i=1}^I (ML_i) = \sum_{i=0}^I (ML_i) \quad (8)$$

$$(L)_T = (L) + (HL) + i(ML_i) \quad (9)$$

where the subscript T refers to "total." Equations 8 and 9 may be expressed as:

$$(M)_T = (M) \left[1 + \sum_{i=1}^I K_i (L)^i \right] \quad (10)$$

and

$$(L)_T = (L)(1 + (H)/K_a) + (M) \sum_{i=1}^I iK_i(L)^i \quad (11)$$

respectively.

The average number of ligands bound to the metal per metal ion in solution may be expressed as follows:

$$\bar{n} = \left[(L)_T - (L)(1 + (H)/K_a) \right] / (M)_T \quad (12)$$

Upon elimination of (M) from equations 10 and 11, the expression for \bar{n} becomes:

$$\bar{n} = \frac{\sum_{i=1}^I iK_i(L)^i}{1 + \sum_{i=1}^I K_i(L)^i} \quad (13)$$

This function which expresses the relationship between \bar{n} and (L) is called the formation function of the system.

If the value of \bar{n} can be obtained from equation 12, the problem of ascertaining the stability constants of the system is reduced to solving a system of I simultaneous equations. The value of \bar{n} can be determined from equation 12 if the concentration of free ligand is so much smaller than the total that their difference is defined.

Procedure and results

The extremely low solubility of the nickel(II)-vic-dioxime complexes precludes the determination of the stability constants by pH measurements in aqueous solution.

Charles and Freiser (18) determined the stability constant of nickel(II) dimethylglyoxime from a knowledge of the \bar{n} and $\log(L)$ values. If \bar{n} is plotted against $\log(L)$, the values of k_1 and k_2 at $\bar{n} = 0.5$ and 1.5 , respectively, are numerically equal to the corresponding values of $\log(L)$. Charles and Freiser found that the values for the step-wise stability constants were nearly equal. In fact the value of $\log(L)$ at $\bar{n} = 0.5$ and 1.5 differed by less than one logarithm unit. When the difference between $\log(L)$ values at $\bar{n} = 0.5$ and 1.5 are small, the formation curve may not be the best method for the evaluation of the system. Dyrssen, *et al.* (21) recalculated the data of Charles and Freiser and found that k_2 is larger than k_1 . The calculations performed by Dyrssen using solubility and distribution data give no evidence for the 1:1 complex of nickel dimethylglyoxime in the system. Thus the formation of the complex which contains two moles of dimethylglyoxime per mole of nickel is favored.

The stability constant of nickel(II) ethylmethylglyoxime was determined in 50% dioxane-50% water (v/v) and 75% dioxane-25% water (v/v) and the stability constant of nickel(II) 4-isopropylglyoxime was determined in 75% dioxane-25% water (v/v).

A dioxane-water solvent was chosen because it dissolved all of the nickel(II)-vic-dioxime complexes studied. The ionic strength in all of the titrations was controlled at 0.1

with sodium perchlorate.

The acid dissociation constants of the vic-dioximes were measured under the same conditions under which the metal and the ligand were titrated. A known amount of vic-dioxime was titrated with standard sodium hydroxide. From a knowledge of the amount of base added and the pH of the solution, the acid dissociation constant was calculated. In order to avoid the neutralization of more than one of the dioxime hydrogens, only about one tenth mole of base per mole of vic-dioxime was added. During the titration, increments of dioxane were added in order to keep the dioxane content constant. According to Ringbom (40), the corrections to be applied to activity coefficients for a small change in ionic strength can be neglected when the ionic strength is 0.1 or higher. The change in volume of the solutions from the addition of dioxane and sodium hydroxide was not greater than 4% in any case. Nitrogen, saturated with water vapor, was passed over the solutions during the titrations. The magnetic stirrer used for mixing was turned off during the actual measurements of pH. The pK_{NH} (basicity of the oxime nitrogen) was determined for each vic-dioxime studied by titrating a known amount of vic-dioxime with standard acid. In all cases the pK_{NH} was less than two which indicated negligible basicity of the oxime nitrogen.

The values of \bar{n} and (L) were determined by titrating a

known amount of ligand at an ionic strength of 0.1 in dioxane-water with standard sodium hydroxide. Increments of dioxane were added in order to keep the dioxane content constant. The change in volume of the solution was not greater than 4% in any titration; no corrections were made for changes in ionic strength. A nitrogen atmosphere was maintained over all the solutions which were used. A second titration was carried out under the same conditions and using the same amounts of reagents with the exception that the second solution contained nickel(II) ions. The difference in the amount of base required to reach the same pH in the two titrations, ΔV , was taken as the amount of ligand bound to the nickel. This assumption is valid if there is a great excess of ligand over the metal ion so that (L) is negligible in comparison with $(HL)_T - (L)_{\text{complexed}}$. The hydrolysis of the nickel(II) ion is not involved in the equilibria because all the complexes are formed at pH values which are lower than the region for the hydrolysis of nickel(II) ions. Achenza (1) reports that the pK for the first hydrolysis constant of nickel(II) at 25° is 10.92. No precipitation of the metal-ligand complex occurred during any of the titrations. ■

Values for \bar{n} were calculated from the amount of ligand complexed and the total analytical concentration of nickel(II) ions in solution. The concentration of free ligand ions, (L) , in solution was calculated from equation 14.

$$\begin{aligned}
 (L) = K_a(HL)/(H) &\cong \frac{K_a \left[(HL)_T - (NiL) - 2(NiL_2) \right]}{(H)} \\
 &= \frac{K_a \left[(HL)_T - \frac{(\Delta V)N}{V} \right]}{(H)} \quad (14)
 \end{aligned}$$

The stability constants of the system were then determined by substitution into equation 13. For the nickel(II)-vic-dioxime complexes studied here the maximum value of i is 2 and the solution of the formation function is simply the solution of two simultaneous equations. For a single titration, as many values of the stability constants of the system may be calculated as there are values of \bar{n} and (L) . The solution of the equations was obtained with the aid of the IBM electronic digital computer.

The data for the calculation of the stability constants for the nickel(II)-vic-dioxime complexes and the constants are given in Tables 3 to 6. The values of \bar{K}_x and K_x refer to dioxane-water mixtures and water solutions respectively.

Relationship Between Stability in Water and Stability in Mixed Solvents

Theory

The manner in which the stability of metal-ligand complexes differ in water and in organic-aqueous solvents has been investigated by Irving and Rossotti (30).

In the following discussion only the 1:1 metal-ligand

Table 3. Titration of nickel(II) ethylmethylglyoxime mixtures with sodium hydroxide^a

NaOH, ΔV^b	pH	\bar{n}	$-\log (L)$
0.90	3.45	0.461	12.23
1.10	3.51	0.563	12.18
1.20	3.53	0.615	12.16
1.30	3.56	0.666	12.13
1.40	3.57	0.717	12.13
1.60	3.62	0.819	12.08
1.70	3.64	0.871	12.06
1.80	3.66	0.922	12.05
2.00	3.72	1.024	11.99
2.20	3.78	1.127	11.94
2.40	3.84	1.229	11.88
2.60	3.88	1.331	11.85
2.80	3.96	1.434	11.77
3.00	4.05	1.536	11.69

^a75% dioxane-25% water, $\mu = 0.1$, $t = 25^\circ$, (HL) = $7.67 \times 10^{-3} \text{M.}$, $(\text{Ni})_T = 2.937 \times 10^{-4} \text{M.}$, $(\text{NaOH}) = 0.01504 \text{M.}$

^bThe difference in volume of sodium hydroxide solution required to titrate the ligand alone and the nickel(II)-ligand mixture to the same pH.

Table 4. Stability constants for nickel(II) ethylmethylglyoxime^a

	$\log \bar{K}_1$	$\log \bar{K}_2$
	10.90	23.92
	9.71	23.95
	10.88	23.98
	10.46	23.46
	10.89	23.99
	9.98	24.00
	11.73	24.04
	9.94	23.95
	11.02	23.93
	9.92	23.97
Average	10.41 ± 0.52	23.97 ± 0.03

^a75% dioxane-25% water, $\mu = 0.1$, $t = 25^\circ$.

complexes and the proton ligand complexes are considered.

The formation constant takes the form



$$K = (ML)(H)/(M)(HL) = {}^cK_{ML} {}^cK_a \quad (16)$$

where K_{ML} is the stability constant of the metal-ligand complex and K_a is the acid dissociation constant. Charges

Table 5. Titration of nickel(II) 4-isopropylinoxime with sodium hydroxide^a

NaOH, ΔV^b	pH	\bar{n}	$-\log (L)$
0.80	4.35	0.345	10.50
1.00	4.37	0.431	10.48
1.20	4.39	0.517	10.46
1.40	4.41	0.603	10.44
1.60	4.44	0.689	10.41
1.80	4.47	0.776	10.38
2.00	4.51	0.862	10.34
2.20	4.54	0.943	10.31
2.40	4.60	1.034	10.25
2.60	4.68	1.120	10.17
2.80	4.76	1.207	10.09
3.00	4.84	1.292	10.01
3.20	4.92	1.379	9.93
3.40	5.00	1.464	9.85
3.60	5.10	1.55	9.55

^a75% dioxane-25% water, $\mu = 0.1$, $t = 25^\circ$, $(\text{NaOH}) = 0.001265 \text{ M.}$, $(\text{HL}) = 2.75 \times 10^{-3} \text{ M.}$, $(\text{Ni})_T = 1.47 \times 10^{-5} \text{ M.}$

^bThe difference in volume of sodium hydroxide required to titrate the ligand alone and the nickel(II)-ligand mixture to the same pH.

Table 6. Stability constants of nickel(II) 4-isopropyl-nioxime^a

	$\log \bar{K}_1$	$\log \bar{K}_2$
	9.99	20.30
	9.83	20.44
	9.89	20.34
	9.33	20.36
	9.88	20.87
	10.24	20.46
	10.18	20.42
	10.11	20.36
Average	10.06 ± 0.31	20.44 ± 0.18

^a75% dioxane-25% water, $\mu = 0.1$, $t = 25^\circ$.

on the ions are omitted for simplicity. $c_{K_{ML}}$ and c_{K_a} are expressed in liters/mole and if, for each species s , the partial molar free energy is denoted by F_s , and the activity coefficient is designated by γ_s , the following relationship exists

$$\ln c_{K_{ML}} = - \ln c_{K_a} + 1/RT(F_M^\circ - F_{ML}^\circ - F_H^\circ + F_{HL}^\circ) + \ln (\gamma_M \gamma_{HL} / \gamma_{ML} \gamma_H) \quad (17)$$

Equation 17 refers to aqueous solution. The analogous

equation in mixed aqueous-organic solvent may be expressed by

$$\ln c_{ML}^{\bar{K}} = - \ln c_{a}^{\bar{K}} + 1/RT(\bar{G}_M^{\circ} - \bar{G}_{ML}^{\circ} - \bar{G}_H^{\circ} + \bar{G}_{HL}^{\circ}) \\ + \ln (\bar{\gamma}_M \bar{\gamma}_{HL})/(\bar{\gamma}_{ML} \bar{\gamma}_H) \quad (18)$$

where $c_{ML}^{\bar{K}}$ refers to the constant in mixed aqueous-organic solvent, \bar{G}_s° is the partial molar free energy in mixed solvent and $\bar{\gamma}_s$ denotes the activity coefficient in mixed solvent. \bar{G}_s and \bar{F}_s° are related by

$$\bar{G}_s - \bar{F}_s^{\circ} = \bar{F}_s^{\circ}(\text{transfer}) - RT \ln \gamma_{s(o)} \quad (19)$$

where $\bar{F}_s^{\circ}(\text{transfer})$ is the partial molar free energy of transfer of the solute species, s, at infinite dilution from water to the binary mixed solvent, and $\gamma_{s(o)}$ is the activity coefficient of the species, s, at infinite dilution in water. Furthermore, Irving and Rossotti (29) expressed $\bar{F}_s^{\circ}(\text{transfer})$ by

$$\bar{F}_s^{\circ}(\text{transfer}) = n_x t_s \quad (20)$$

where n_x is the mole fraction of the organic content and t_s is a constant for each combination of solute species and organic solvent. Equation 18 may be written as

$$\ln c_{ML}^{\bar{K}} = - \ln c_{a}^{\bar{K}} + 1/RT(\bar{F}_M^{\circ} - \bar{F}_{ML}^{\circ} - \bar{F}_H^{\circ} + \bar{F}_{HL}^{\circ}) \\ + n_x(t_M - t_{ML} - t_H + t_{HL}) \\ + \ln (\bar{\gamma}_M \bar{\gamma}_{HL}/\bar{\gamma}_{ML} \bar{\gamma}_H) \quad (21)$$

If equation 20 is valid for the species H, L, HL, M, and ML, the following equations may be written

$$\begin{aligned}
 - \ln c_{K_a}^{\bar{K}} + \ln c_{K_a}^{\bar{K}} &= n_x/RT(t_H + t_L - t_{HL}) \\
 &+ \ln \left(\frac{\bar{v}_H \bar{v}_L}{\bar{v}_{HL}} \bigg/ \frac{v_H v_L}{v_{HL}} \right)
 \end{aligned} \tag{22}$$

and

$$\begin{aligned}
 \ln c_{ML}^{\bar{K}} - \ln c_{ML}^{\bar{K}} &= n_x/RT(t_M + t_L - t_{ML}) \\
 &+ \ln \left(\frac{\bar{v}_M \bar{v}_L}{\bar{v}_{ML}} \bigg/ \frac{v_M v_L}{v_{ML}} \right)
 \end{aligned} \tag{23}$$

If equation 22 is valid, a plot of $\log c_{K_a}^{\bar{K}}$ against n_x will be a straight line of intercept $\log c_{K_a}^{\bar{K}}$, provided that the last term in equation 22 is negligible compared to the other terms or is proportional to n_x . In the same manner, $\log c_{ML}^{\bar{K}}$ may be plotted against n_x in order to evaluate $\log c_{ML}^{\bar{K}}$.

The expression for the combination of equations 22 and 23 is

$$\begin{aligned}
 \ln c_{ML}^{\bar{K}} - \ln c_{ML}^{\bar{K}} &= - \ln c_{K_a}^{\bar{K}} + \ln c_{K_a}^{\bar{K}} + n_x/RT(t_M - t_{ML} \\
 &- t_H + t_{HL}) \\
 &- \ln \left(\frac{\bar{v}_{ML} \bar{v}_H}{\bar{v}_M \bar{v}_{HL}} \bigg/ \frac{v_{ML} v_H}{v_M v_{HL}} \right)
 \end{aligned} \tag{24}$$

If the last two terms in equation 24 are negligible compared to the other terms, the equation may be expressed as

$$\log \bar{c}_{K_{ML}} = \log c_{K_{ML}} + (p\bar{c}_{K_a} - p^c K_a) \quad (25)$$

where the logarithms are converted to the base 10 and pK represents the negative logarithm.

The evaluation of the stability of metal-ligand complexes which are sparingly soluble in water may be achieved by plotting $\log \bar{c}_{K_{ML}}$ against n_x and extrapolating to infinite dilution of the organic content. The nickel(II) complexes of the vic-dioximes are not soluble enough in water to determine their stability by plotting $\log \bar{c}_{K_{ML}}$ against n_x . Thus equation 25 was used in order to get an approximation of the stability constants in water.

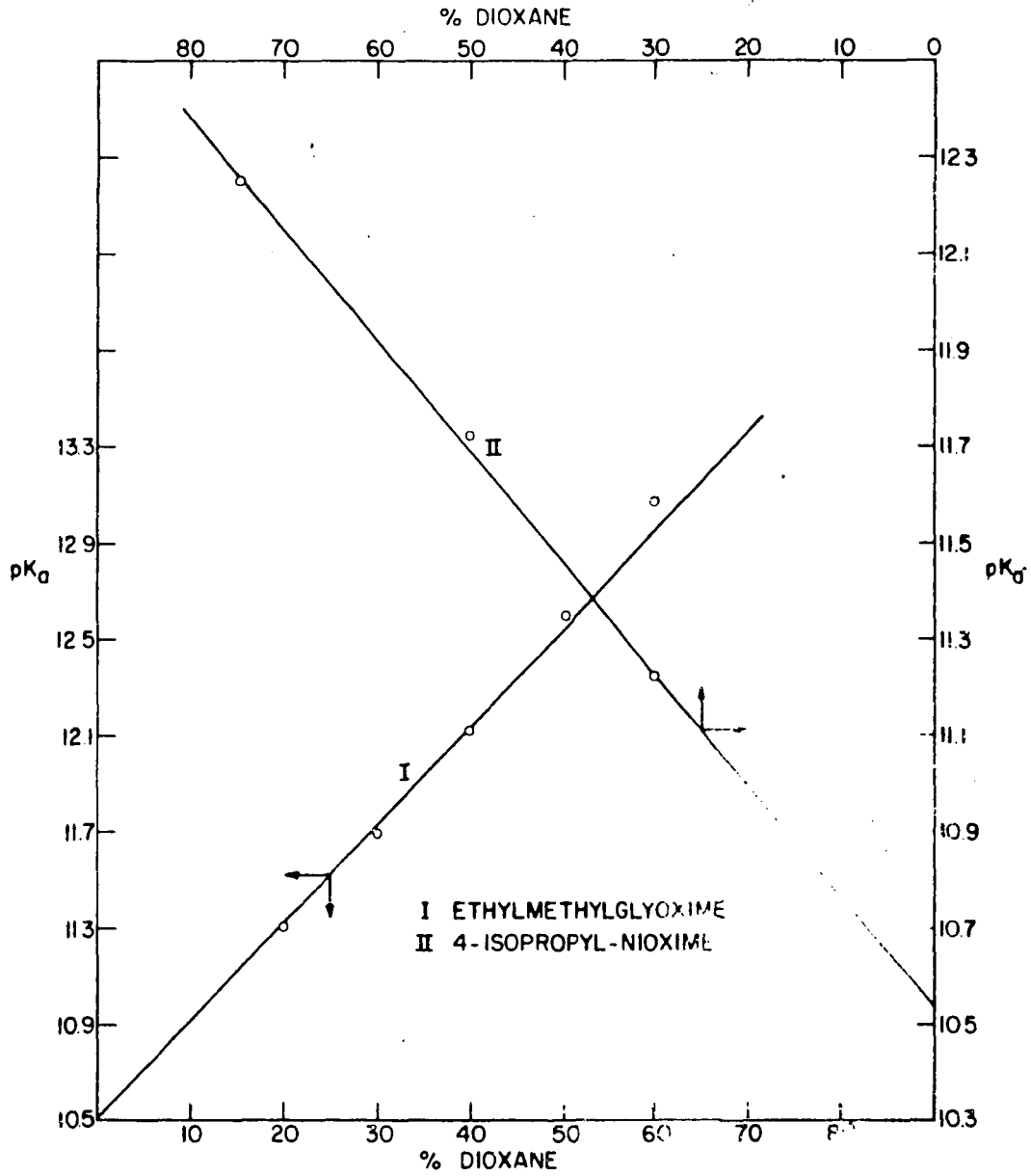
The equations, 15-25, apply only to the 1:1 complexes but approximations for $1/2 \log K_2$ can be obtained by using $1/2 \log \bar{K}_2$.

Procedure and results

In order to use equation 25, the value of $(p\bar{c}_{K_a} - p^c K_a)$ was determined for ethylmethylglyoxime and 4-isopropylnoxime. This was done by plotting $p\bar{c}_{K_a}$ against per cent dioxane and extrapolating to infinite dilution of dioxane. Linear curves were obtained. The curves are given in Figure 1.

The applicability of equation 25 has been demonstrated (2). This was done by determining the stability constants of

Figure 1. Acid dissociation constants of ethylmethylglyoxime and 4-isopropylhydroxime as a function of dioxane concentration



copper(II) and cobalt(II) dimethylglyoxime in water solution, 50% (v/v) aqueous dioxane and 75% dioxane-25% water (v/v). The cobalt and copper complexes of dimethylglyoxime are soluble in water solution. A comparison of the values of $(p^c\bar{K}_a - p^cK_a)$ for dimethylglyoxime as determined experimentally and as determined from the stabilities of copper and cobalt dimethylglyoxime in water and in aqueous-dioxane

Table 7. Stability constants of copper(II) and cobalt(II) dimethylglyoxime complexes in dioxane-water mixtures and values of $(p\bar{K}_a - pK_a)^a$

% Dioxane	$\log K_1$	$1/2 \log K_2$	$(p\bar{K}_a - pK_a)^b$	$(p\bar{K}_a - pK_a)^c$
Copper(II)				
0	9.05	9.25	--	--
50	11.94	11.66	2.41	2.07
75	12.23	12.17	2.92	3.05
Cobalt(II)				
0	8.35	8.49	--	--
50	11.01	10.34	1.85	2.07
75	12.20	11.22	2.73	3.05

^aData taken from reference (2), p. 47.

^bCalculated from equation 25 and values of $1/2 \log \bar{K}_2$.

^cCalculated from experimentally determined values of $p\bar{K}_a$ and pK_a .

mixtures will show that equation 25 is a good approximation for equation 24. Because the vic-dioximes are very similar, if equation 25 is valid for complexes of dimethylglyoxime, it is probably a good assumption that it also applies to the complexes of the other vic-dioximes. The results are given in Table 7.

The acid dissociation constants for ethylmethylglyoxime and 4-isopropyl-nioxime and the approximate over-all stability constants for the nickel(II) complexes in aqueous solution are given in Table 8. The values of the term ($p\bar{K}_a - pK_a$) in Table 7 show that the last two terms in equation 24 are of the order of the experimental error.

Table 8. Acid dissociation constants of vic-dioximes and stability constants of nickel vic-dioximes in water-dioxane mixtures

Complex	pK_a	$\log K_1$	$\log K_2$
Ni(ethylmethylglyoxime)	13.55 ^a	10.41 ^a	23.97 ^a
	10.41 ^b	7.27 ^b	17.26 ^b
Ni(4-isopropyl-nioxime)	12.27 ^a	10.06 ^a	20.44 ^a
	10.53 ^b	8.42 ^b	16.76 ^b

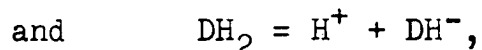
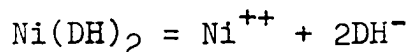
^a75% dioxane.

^bWater solution.

Solubility Product Constants of Some
Nickel(II)-vic-dioxime Complexes

Theory

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



where DH_2 , represents the free dioxime with two ionizable hydrogens. The solubility product constant is given by

$$K_{\text{sp}} = a_{\text{Ni}^{++}} \cdot a_{\text{DH}^-}^2 \quad (26)$$

and the ionization constant by

$$K_a = \frac{a_{\text{H}^+} \cdot a_{\text{DH}^-}}{a_{\text{DH}_2}} \quad (27)$$

The equilibria involved in the solubility product constant are as follows:

$$(\text{Ni})_{\text{T}} = (\text{Ni}) + (\text{Ni}(\text{DH})_2) \quad (28)$$

$$(\text{DH}_2)_{\text{T}} = (\text{DH}^-) + (\text{DH}_2) + 2(\text{Ni}(\text{DH})_2) \quad (29)$$

$$2(\text{Ni})_{\text{T}} = (\text{DH}_2)_{\text{T}} \quad (30)$$

where $(\text{Ni})_{\text{T}}$ is the total amount of nickel present and $(\text{DH}_2)_{\text{T}}$ is the total amount of vic-dioxime present at equilibrium, expressed in moles per liter.

$$(H^+) + 2(Ni^{++}) = (ClO_4^-) + (DH^-) \quad (31)$$

$$(ClO_4^-) = 2(Ni)_T \quad (32)$$

$$(i) = a_i/f_i \quad (33)$$

(i) represents the molar concentration of the species i.

$$\frac{a_{H^+}}{f_{H^+}} + 2(Ni^{++}) = 2(Ni)_T + \frac{a_{DH^-}}{f_{DH^-}} \quad (34)$$

Eliminate $(Ni(DH)_2)$ between equations 28 and 29.

$$2(Ni^{++}) = (DH^-) + (DH_2) \quad (35)$$

Using equation 27 and solving for a_{DH_2} one obtains:

$$a_{DH_2} = (DH_2) \cdot f_{DH_2} = \frac{a_{H^+} \cdot a_{DH^-}}{K_a} \quad (36)$$

Substituting this into equation 35:

$$2(Ni^{++}) = (DH^-) + \frac{a_{H^+} \cdot (DH^-) \cdot f_{DH^-}}{K_a \cdot f_{DH_2}} \quad (37)$$

Eliminate $2(Ni^{++})$ between equations 34 and 37.

$$\frac{a_{H^+} \cdot a_{DH^-}}{K_a \cdot f_{DH_2}} = 2(Ni)_T - \frac{a_{H^+}}{f_{H^+}} \quad (38)$$

$$a_{DH^-} = \frac{K_a \cdot f_{DH_2}}{a_{H^+}} \left[2(Ni)_T - \frac{a_{H^+}}{f_{H^+}} \right] \quad (39)$$

Substituting this expression for a_{DH^-} into equation 34:

$$\frac{2a_{Ni^{++}}}{f_{Ni^{++}}} = 2(Ni)_T - \frac{a_{H^+}}{f_{H^+}} + \frac{K_a \cdot f_{DH_2}}{a_{H^+} \cdot f_{DH^-}} \left[2(Ni)_T - \frac{a_{H^+}}{f_{H^+}} \right] \quad (40)$$

If one neglects the third term in equation 40, which is negligible, and solves for $a_{Ni^{++}}$ the results are:

$$a_{Ni^{++}} = (Ni)_T f_{Ni^{++}} - \frac{a_{H^+} \cdot f_{Ni^{++}}}{2f_{H^+}} \quad (41)$$

Using equations 39 and 41, the solubility product constant can be evaluated.

$$K_{sp} = \frac{K_a^2}{a_{H^+}^2} (2(Ni)_T - (H^+))^2 \quad (42)$$

$$\left[(Ni)_T \cdot f_{Ni^{++}} - \frac{(H^+) \cdot f_{Ni^{++}}}{2} \right]$$

Procedure and results

Nickel perchlorate and the vic-dioxime were mixed in stoichiometric amounts, shaken at room temperature for two hours and the pH measured. Between 0.100 and 1.00 ml. of 0.05874 M. nickel solution was added with a micro-pipet to a solution of the vic-dioxime. The volume of the sample was adjusted by adding a known amount of water. The ionic strength was adjusted by using a solution of sodium perchlorate. The values of the activity coefficients are those reported by Kielland (32). The pH of the mixture was determined without filtering.

Values of the solubility products determined by this method are reported in Tables 9 to 12.

Table 9. Determination of the solubility product of nickel diethylglyoxime at 25^oa

$(\text{Ni})_T \times 10^4$	μ	pH	K_{sp}
2.448	0.0834	4.07	7.81×10^{-25}
2.448	0.0834	4.08	7.77×10^{-25}
2.448	0.0834	4.03	6.05×10^{-25}
1.469	0.100	4.26	7.87×10^{-25}
		Average	7.38×10^{-25}

^aThe acid dissociation constant of diethylglyoxime is 2.14×10^{-11} (2).

Table 10. Determination of the solubility product of nickel ethylmethylglyoxime at 25^oa

$(\text{Ni})_T \times 10^4$	μ	pH	K_{sp}
1.469	0.10	4.60	5.65×10^{-24}
1.469	0.10	4.54	4.02×10^{-24}
1.469	0.10	4.58	5.01×10^{-24}
1.469	0.10	4.60	5.65×10^{-24}
1.469	0.05	4.64	8.38×10^{-24}
1.469	0.10	4.60	5.65×10^{-24}
		Average	5.73×10^{-24}

^aThe acid dissociation constant of ethylmethylglyoxime is 3.89×10^{-11} (this work).

Table 11. Determination of the solubility product of nickel dipropylglyoxime at 25°a

$(\text{Ni})_T \times 10^5$	μ	pH	K_{sp}
2.129	0.10	5.02	1.06×10^{-26}
2.129	0.10	5.07	2.26×10^{-26}
2.129	0.05	5.23	6.15×10^{-26}
2.129	0.025	5.23	9.11×10^{-26}
2.129	0.010	5.22	8.53×10^{-26}
2.129	0.005	5.14	7.28×10^{-26}
		Average	6.67×10^{-26}

^aThe acid dissociation constant of dipropylglyoxime is 1.55×10^{-11} (2).

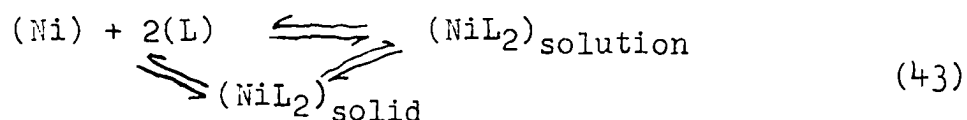
Table 12. Determination of the solubility product of nickel 4-isopropylnoxime at 25°a

$(\text{Ni})_T \times 10^4$	μ	pH	K_{sp}
2.937	0.10	3.35	1.02×10^{-28}
2.937	0.05	3.34	1.77×10^{-28}
2.937	0.025	3.33	1.23×10^{-28}
1.469	0.050	3.65	1.53×10^{-28}
		Average	1.39×10^{-28}

^aThe acid dissociation constant of 4-isopropylnoxime is 2.95×10^{-11} (this work).

Intrinsic Solubility

The over-all stability constant, the solubility product and the intrinsic solubility constant for the nickel(II)-vic-dioxime complexes are related as follows:



The equilibrium constants are:

$$K_{\text{sp}} = (\text{Ni})(\text{L})^2 \quad (44)$$

$$K_2 = \frac{(\text{NiL}_2)_{\text{solution}}}{(\text{Ni})(\text{L})^2} \quad (45)$$

$$K_s = K_s'(\text{NiL}_2)_{\text{solid}} = (\text{NiL}_2)_{\text{solution}} \quad (46)$$

where K_{sp} is the solubility product constant, K_2 is the over-all stability constant and K_s is the intrinsic solubility constant. The relationship among the constants may be represented by

$$K_s = K_{\text{sp}}K_2 \quad (47)$$

The intrinsic solubility constants for the nickel(II) complexes of dimethylglyoxime, nioxime, 3-methylnioxime, 4-methylnioxime and heptoxime have been calculated using values of K_{sp} from the work of banks and Barnum (4) in conjunction with the values of K_2 from the work of the author (2). The K_2 values for the nickel complexes of diethylglyoxime and

dipropylglyoxime as reported by the author are used to calculate K_s . The values of the intrinsic solubility and the values of the nickel-nickel bond distance as reported by Banks and Barnum (4) are given in Table 13.

Table 13. Values of the intrinsic solubility, nickel-nickel bond length, solubility product and over-all stability constant for nickel(II) complexes of several vic-dioximes

<u>Vic</u> -dioxime	pK_s	Ni--Ni bond length in A. U. ^a	pK_{sp}	$\log K_2$
Dimethylglyoxime	6.66	3.233	23.66	17.00
Ethylmethylglyoxime	5.70	- ^b	23.27	17.57
Diethylglyoxime	6.96	- ^c	24.21	17.17
Dipropylglyoxime	8.02	- ^c	25.14	17.12
4-Isopropylnoxime	11.08	3.19	27.84	16.76
Nioxime	11.06	3.237	28.39	17.34
4-Methylnoxime	10.32	3.24	28.25	17.94
3-Methylnoxime	9.34	3.47	27.62	18.28
Heptoxime	7.20	3.596	26.64	19.44

^aValues taken from work of Banks and Barnum (4).

^bDoes not form nickel-nickel bonds (24).

^cCrystal structure has not been determined.

Crystal Structures

Frasson and Panatoni (24) have determined the crystal structure of nickel ethylmethylglyoxime. They found that it is monoclinic and the nickel atoms are too far apart to participate in nickel-nickel bonding.

An examination of the powder x-ray diffraction photographs of nickel diethylglyoxime and nickel dipropylglyoxime indicates that they too have a different crystal structure than nickel dimethylglyoxime and their structure is not the same as nickel ethylmethylglyoxime. Furthermore, nickel diethylglyoxime and nickel dipropylglyoxime have different crystal structures. In order to determine the distances between nickel atoms in the crystal, the crystal structure must be known.

Spectra of Some Nickel(II)-vic-dioxime Complexes

Colloidal suspensions

If a nickel(II)-vic-dioxime complex is prepared in water in the presence of a protective colloid, such as gum arabic or gelatin, then a stable colloidal suspension of the complex is obtained. These suspensions have been studied by Hooker (29), who determined that the size of the particles is about 20 x 2000 millimicrons.

A known amount of nickel perchlorate was added to a volumetric flask and 5 ml. of 10% gum arabic was added. The

vic-dioxime was then added in about 50% excess, and a few drops of 1 M. ammonium hydroxide. The solution was then diluted to the mark with water. The absorption spectrum was then measured on a Cary Model 14 recording spectrophotometer using 1-cm. cuvettes.

Chloroform solution

An accurately weighed quantity of the nickel(II)-vic-dioxime complex was dissolved in chloroform and diluted to the mark in a volumetric flask. The solution was then scanned on the Cary Model 14 recording spectrophotometer using 1-cm. cells.

The absorption bands and the molar absorptivities are reported in Tables 14 and 15. The absorption spectra for the complexes in colloidal suspension and in chloroform solution are reported in Figures 2, 3 and 4.

Table 14. Absorption maxima and molar absorptivities of colloidal suspensions

Complex	$\lambda_{\max}(\mu)$	$\epsilon \times 10^{-3}$
Ni(ethylmethylglyoxime)	506	2.375
Ni(diethylglyoxime)	462	4.56
Ni(dipropylglyoxime)	445	2.25

Figure 2. Absorption spectra of nickel(II) ethylmethylglyoxime

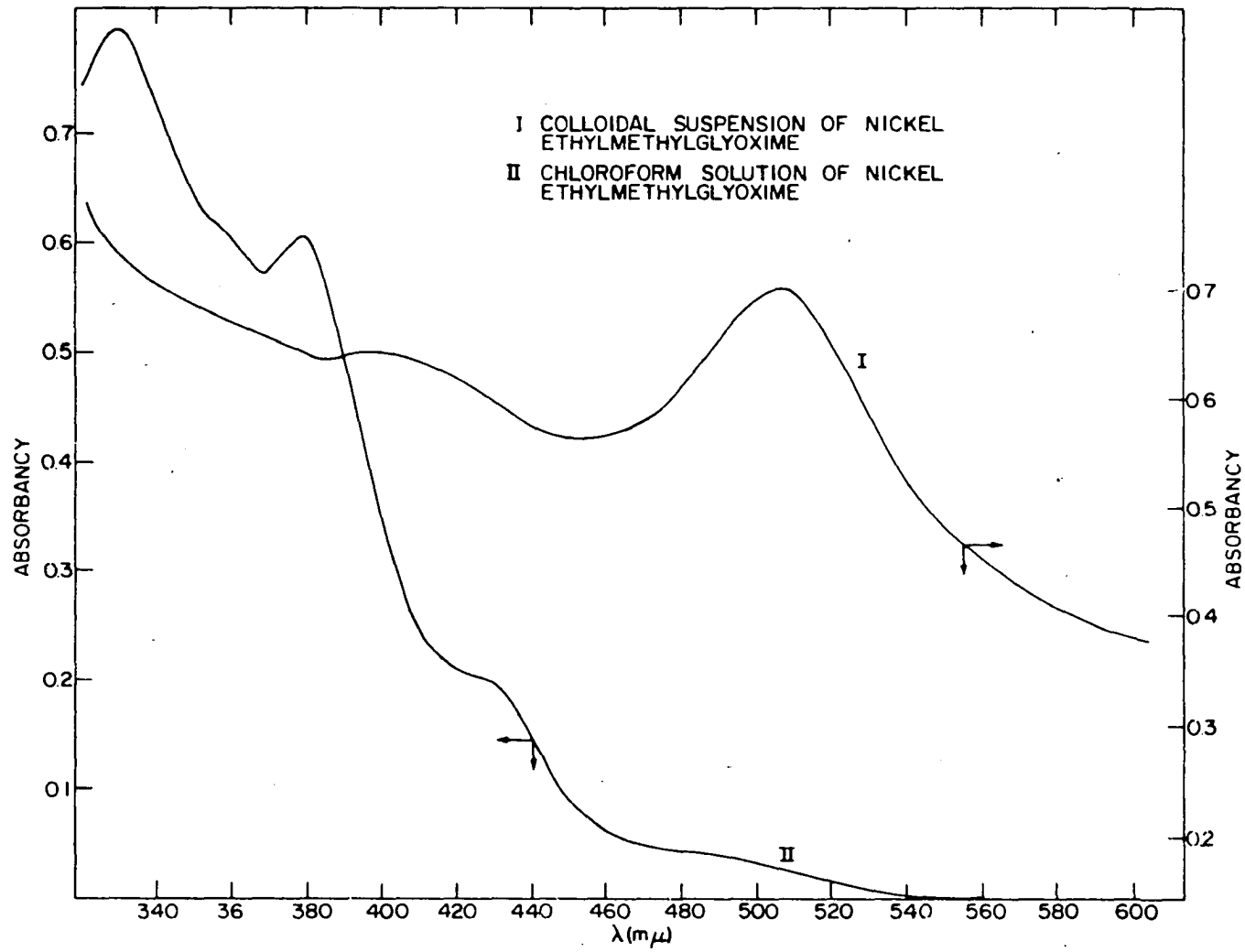


Figure 3. Absorption spectra of nickel(II) dipropylglyoxime

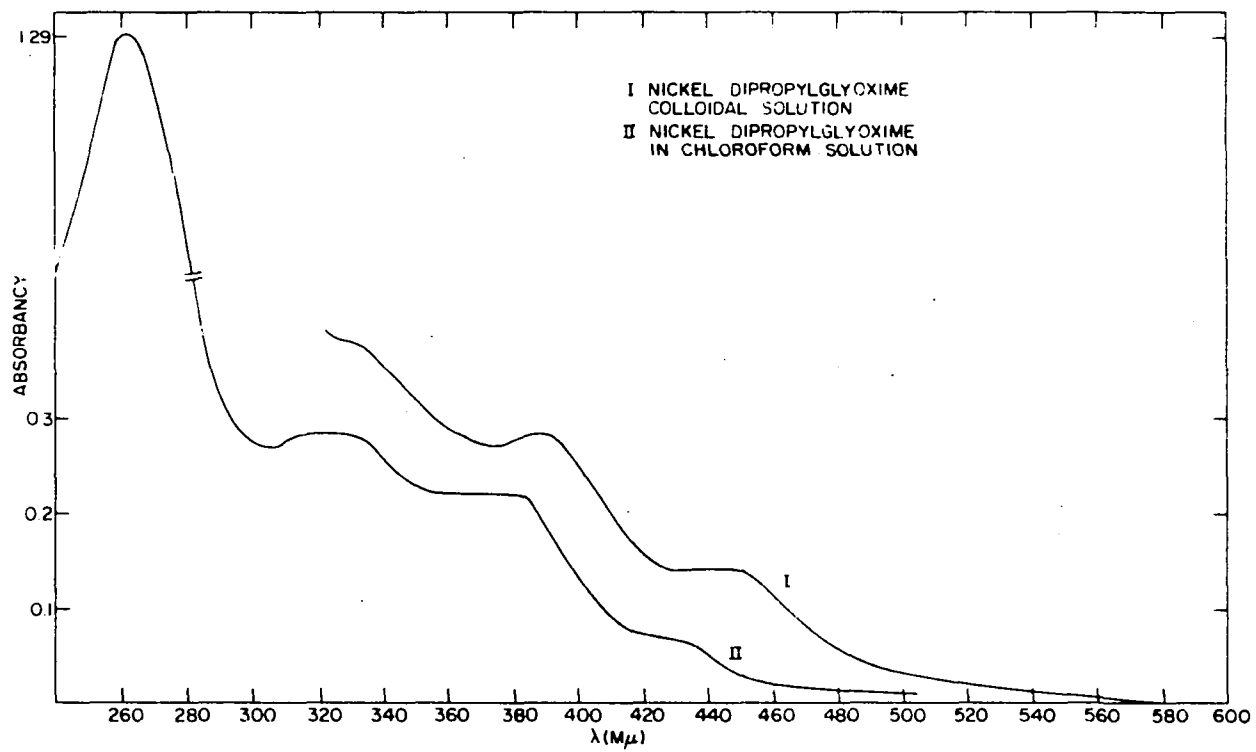


Figure 4. Absorption spectra of nickel(II) diethylglyoxime

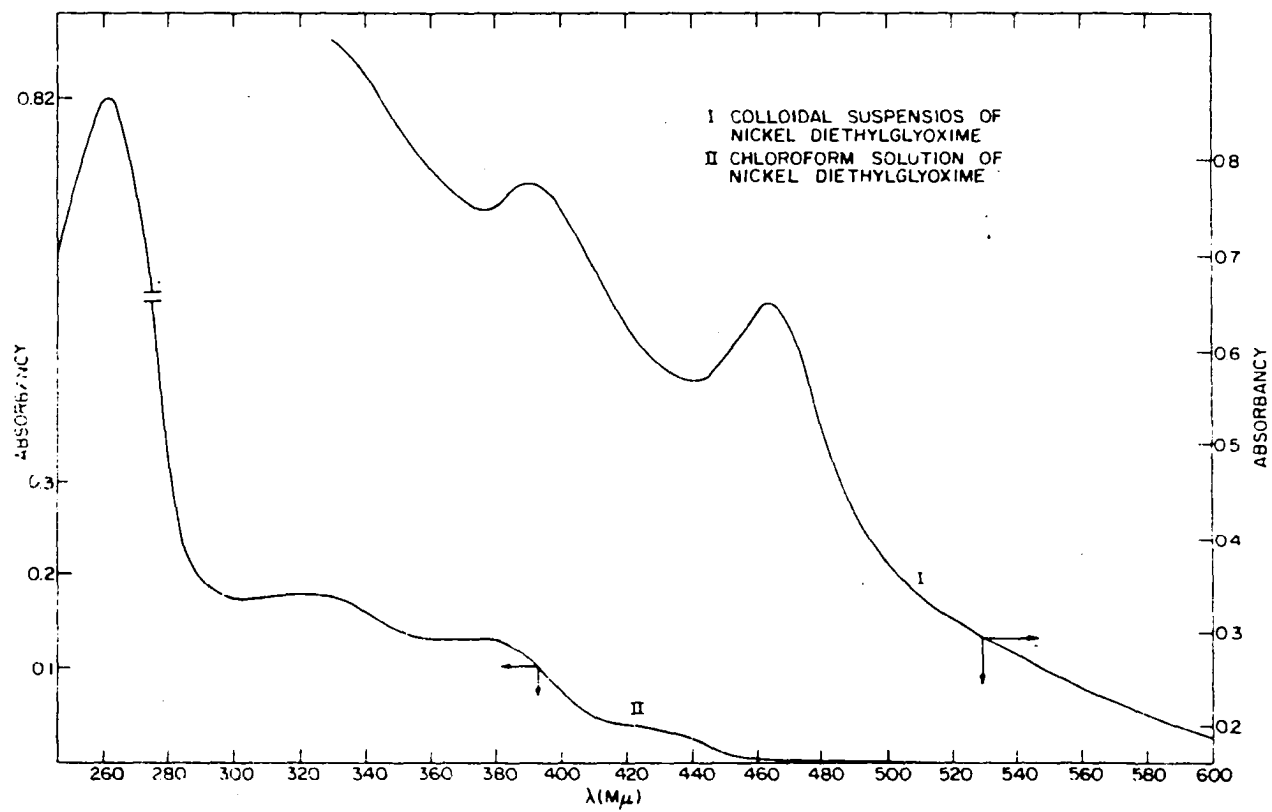


Table 15. Absorption maxima and molar absorptivities in chloroform solution

Complex	λ_{\max} (m μ)	$\epsilon \times 10^{-3}$
Ni(ethylmethylglyoxime)	377	3.74
	328	4.874
Ni(diethylglyoxime)	380	3.39
	325	4.56
	261	2.13
Ni(dipropylglyoxime)	380	3.90
	325	5.00
	261	2.29

Heats of Solution

Theory

In order for the difference in the heats of solution of two compounds in the same solvent to be interpreted as the difference in their crystal energies, there should be little solvent-solute interaction, or the degree of solvent-solute interaction should be the same for both compounds. The heats of solution which one measures experimentally represents the heat of fusion and the heat of solvation. Any interaction of the solvent with the solute will tend to decrease the over-all heat measured.

Fleischer (22) has determined the heats of solution of nickel dimethylglyoxime and copper dimethylglyoxime in water, chloroform, benzene and n-heptane. He suggests that benzene and heptane are sufficiently inert toward the two complexes so that the differences in their heat of solution in each solvent represents the difference in their crystal energies.

The crystal structure of nickel ethylmethylglyoxime (24) indicates that it does not form nickel-nickel bonds in the crystal state. Godycki and Rundle (26) proposed that the stability of the crystal of nickel dimethylglyoxime is increased by the presence of metal-metal bonds in the crystal. Copper dimethylglyoxime does not form metal-metal bonds but it does form copper-oxygen bonds (23). From his solubility data and the differences in the heats of solution of copper and nickel dimethylglyoxime, Fleischer concluded that the nickel-nickel bond in nickel dimethylglyoxime, if it exists, must be extremely weak.

Because nickel ethylmethylglyoxime does not form nickel-nickel bonds, the difference in the crystal energies between the nickel complexes of dimethylglyoxime and ethylmethylglyoxime should be an indication of the maximum strength of the nickel-nickel bond.

The heat of solution of nickel ethylmethylglyoxime was determined from the temperature dependence of the solubility in the following solvents: water, chloroform, benzene,

n-heptane and carbon tetrachloride. The heat of solution of nickel dimethylglyoxime was determined in carbon tetrachloride.

The standard state for each solute in the calculations was the mole fraction one and 298°K. The standard free energy, enthalpy and entropy changes were calculated from the following expressions:

$$\Delta F^\circ = - RT \ln X_2 \quad (47)$$

$$\ln X_2/X_2^1 = \Delta \bar{H}^\circ(T_2 - T_1)/RT_1T_2 \quad (48)$$

$$\Delta S^\circ = (\Delta H^\circ - \Delta F^\circ)/T \quad (49)$$

where X_2 is the mole fraction at T_2 and X_2^1 is the mole fraction at T_1 . 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.

Procedure and results

A constant temperature water bath equipped with a micro temperature regulator was used for equilibration of the solutions. All the mixtures were agitated periodically while suspended in the bath. The mixtures in n-heptane and carbon tetrachloride were agitated continuously with a mechanical shaker. For several of the solutions, equilibrium was approached from a higher and a lower temperature. The results were the same within experimental error. The temperatures at which the solubilities were measured were 25° and 33.3° except that the higher temperature used for the

solubility of nickel ethylmethylglyoxime in chloroform was 32°.

Pipets equipped with filters were used for sampling the solutions. Quantitative dilutions of the samples were made immediately. A time interval of about 24 hours was sufficient in order to assure that equilibrium had been reached.

An experimental check on the procedure was obtained by determining the solubility of nickel dimethylglyoxime in chloroform and comparing with the value obtained by Fleischer (22). The results agreed within experimental error.

The analytical procedures for the different solutions were the same as those used by Fleischer except for minor variations.

Solubility in water The analytical curve was established by dissolving weighed amounts of nickel ethylmethylglyoxime in chloroform and reading the absorbancy on a Beckman DU spectrophotometer at 377 μ and 328 μ . A plot of concentration against absorbancy yielded a straight line.

The samples were extracted with 5 ml. of chloroform and the absorbancy measured at 377 and 328 μ . A blank was prepared in the same manner.

Solubility in chloroform The same analytical curve was used as was described for the solubility in water.

Aliquots of the sample were diluted in volumetric flasks after filtering and the absorbancy measured at 377 μ .

Solubility in benzene The calibration curve was established by dissolving accurately weighed amounts of the nickel ethylmethylglyoxime in benzene and diluting to the mark in volumetric flasks. The absorbancy was measured at 379 m μ . A linear relationship between concentration and absorbancy was established.

The samples were quantitatively diluted and the absorbancy measured at 379 m μ .

Solubility in heptane The calibration curve was the same as that described for the solubility in water.

Known volumes of the sample solution were placed in a separatory funnel. The flasks were rinsed with 10 ml. of 1 N. hydrochloric acid and several portions of distilled water which were added to the separatory funnel. After extraction, the aqueous layer was treated with 10 ml. of saturated ethylmethylglyoxime and the pH adjusted to about 6 with ammonium hydroxide. This was then extracted with 5 ml. of chloroform. The absorbancy of the chloroform solution was measured at 328 m μ and 377 m μ . A separate reagent blank was used.

Solubility in carbon tetrachloride The calibration curve for nickel ethylmethylglyoxime was obtained by weighing a known amount of nickel ethylmethylglyoxime and dissolving in a volumetric flask then diluting to the mark. Quantitative dilutions were made the absorbancy measured at 378 m μ . It

was found that a linear relationship exists between concentration and absorbancy.

The experimental solutions were analyzed by taking an aliquot and diluting to the mark in a volumetric flask. The absorbancy was then read at 378 m μ .

The experimental solutions of nickel dimethylglyoxime were analyzed by the same procedure as were the solutions of nickel ethylmethylglyoxime in n-heptane.

The results are reported in Tables 16 and 17. The solubilities reported at each temperature are the average of at least two determinations.

Table 16. Solubility of nickel ethylmethylglyoxime and nickel dimethylglyoxime^a

Solvent	Complex	- log X ₂				
		20°	25°	32°	33.3°	35°
H ₂ O	Ni(DMG) ₂ ^b		7.72			7.49
	Ni(EMG) ₂ ^c		7.30		7.23	
CHCl ₃	Ni(DMG) ₂	4.57	4.43			
	Ni(EMG) ₂		3.04	3.00		
C ₆ H ₆	Ni(DMG) ₂		5.17			6.00
	Ni(EMG) ₂		3.63		3.41	
<u>n</u> -Heptane	Ni(DMG) ₂		7.44			7.08
	Ni(EMG) ₂		6.74		5.62	
CCl ₄	Ni(DMG) ₂		6.24		5.92	
	Ni(EMG) ₂		4.10		4.03	

^aValues for Ni(DMG)₂ in all solvents except CCl₄ were taken from Fleischer (22).

^bNickel dimethylglyoxime.

^cNickel ethylmethylglyoxime.

Table 17. Thermodynamic quantities for nickel dimethylglyoxime and nickel ethylmethylglyoxime^a

Solvent	Solute ^b	ΔH° kcal.	$\Delta(\Delta H^\circ)$ kcal.	ΔF° ^c kcal.	ΔS° ^c
H ₂ O	Ni(DMG) ₂	10.25		10.53	- 0.94
	Ni(EMG) ₂	3.43	- 6.82	9.96	-21.9
CHCl ₃	Ni(DMG) ₂	6.1		6.06	+ 0.15
	Ni(EMG) ₂	2.88	- 3.2	4.15	- 4.25
C ₆ H ₆	Ni(DMG) ₂	7.27		7.05	+ 0.73
	Ni(EMG) ₂	7.00	- 0.27	4.95	+ 6.88
<u>n</u> -Heptane	Ni(DMG) ₂	15.1		10.15	+16.62
	Ni(EMG) ₂	5.8	- 9.3	9.19	-11.39
CCl ₄	Ni(DMG) ₂	15.3		8.50	+22.8
	Ni(EMG) ₂	4.0	-11.3	5.59	- 5.34

^aValues are calculated from data in Table 16.

^bNi(DMG)₂ = nickel dimethylglyoxime, Ni(EMG)₂ = nickel ethylmethylglyoxime.

^cCalculated for 25°.

RESULTS AND DISCUSSION

Stability Constants

The acid dissociation constants of the ligands and the stability constants of some nickel(II)-vic-dioxime complexes are tabulated in Table 18. A comparison of the over-all stability constants for the nickel(II)-vic-dioxime complexes shows that all have values of the same order of magnitude. This is to be expected because the nature of the ligand does not change very much.

Generally, when a metal forms a complex with a series of similar ligands, a nearly linear relationship is observed between the acid dissociation constants of the ligands and the stability constants of the complexes. If one considers the alicyclic and aliphatic series separately, within experimental error one observes that the increase in stability constant follows a decrease in the acid dissociation constant. The nickel(II)-vic-dioxime complexes should not be expected to exhibit a strict relationship between the acid dissociation constant and the stability constant for a series of complexes because the nature of the bonding between the proton-ligand and the metal-ligand are not the same. In the case of the proton-ligand, the bonding is between a hydrogen and an oxygen while in the case of the metal-ligand, the bonds are between nitrogen and metal atoms. Thus the stability of the metal-ligand complex depends in part upon the ability of the

Table 18. Acid dissociation constants of some vic-dioximes and the stability constants of their nickel complexes in water solution^a

<u>Vic</u> -dioxime	pK _a	log K ₂
Dimethylglyoxime	10.48	17.00
Ethylmethylglyoxime	10.41*	17.26*
Diethylglyoxime	10.67	17.17
Dipropylglyoxime	10.81	17.12
4-Isopropylnoxime	10.53*	16.76*
Noxime	10.55	17.34
3-Methylnioxime	10.61	18.28
4-Methylnioxime	10.54	17.94
Heptoxime	10.71	19.44

^aValues marked with an asterisk (*) were measured in this work. All other values were taken from previous work by the author (2).

nitrogens to donate electron pairs to the metal.

It has been demonstrated (2) that equation 25 gives an approximation which is within experimental error of the relationship between stability in water and stability in dioxime-water mixtures.

Solubility Product Constants and Intrinsic Solubility

The values of the solubility product constants and the intrinsic solubility constants are reported in Table 13.

Godycki and Rundle (26) suggested that the insolubility of nickel dimethylglyoxime in water is due in part to the presence of nickel-nickel bonding which increases the stability of the crystal. Banks and Barnum (4) measured the nickel-nickel bond distance in a series of nickel vic-dioximes and tried to correlate the solubility with nickel-nickel bond distance. The results of this work indicated that there is a trend of increased solubility with increasing nickel-nickel bond length.

From equation 47, $K_s = K_{sp}K_2$, one can see that the solubility product constant is a function of the intrinsic solubility constant and the stability constant. The stability constant is not dependent upon the lattice energy of the crystal and thus there would be no reason why the solubility product constant should correlate with the nickel-nickel length. The intrinsic solubility, which represents the equilibria between the dissolved solute and the crystal is the constant which one would expect to be dependent upon the forces which affect the lattice energy of the crystal.

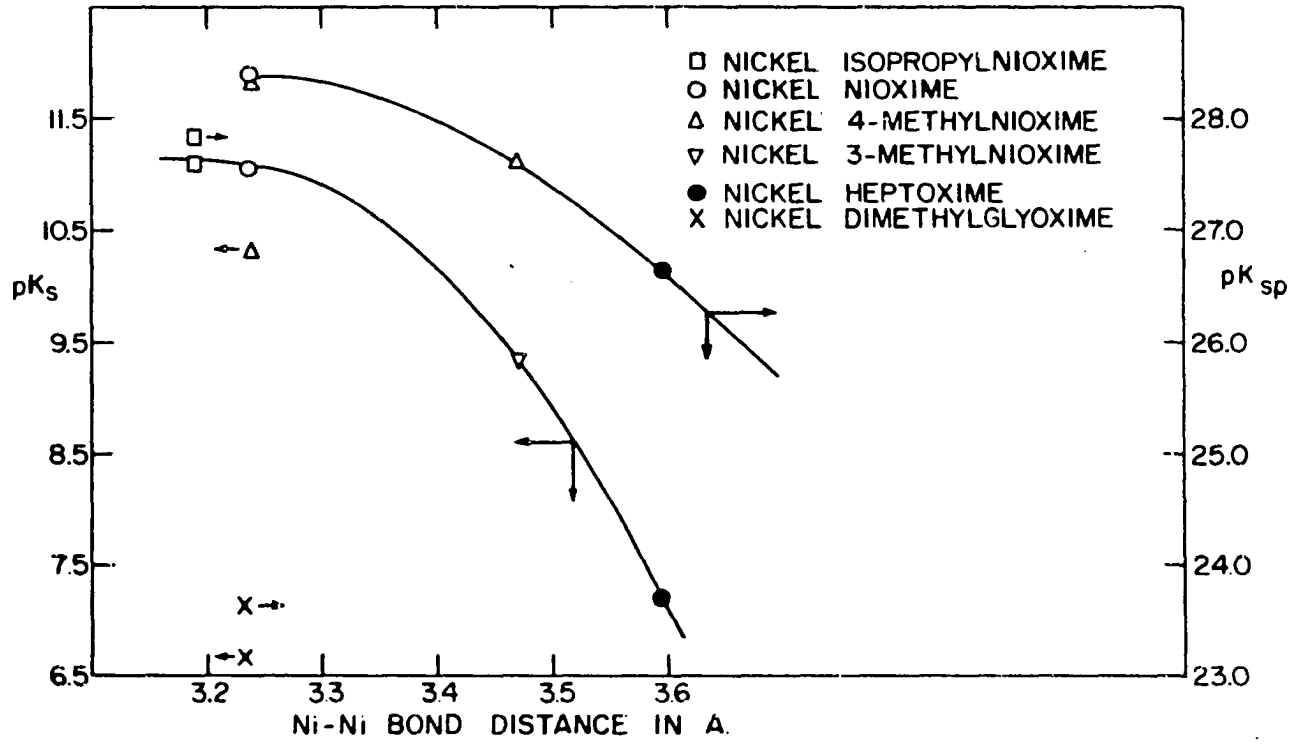
When one considers only the alicyclic vic-dioximes and plots the intrinsic solubility constant against the nickel-nickel bond distance for the complex with nickel, a smooth curve is obtained in which only nickel 4-methylglyoxime is not on the curve. If the nickel-nickel bond distance is plotted against the solubility product, nickel-4-isopropylglyoxime and

nickel nioxime are off the curve. The results are shown in Figure 5.

No reason can be given for the failure of nickel 4-methylnioxime to fall on the curve except possibly an error in the nickel-nickel bond distance or an error in the intrinsic solubility or both. When one considers nickel dimethylglyoxime, the situation is a bit more difficult to understand. While the nickel-nickel bond in nickel dimethylglyoxime is approximately the same length as in nickel nioxime, the water solubility of nickel dimethylglyoxime is much higher. It is possible that nickel dimethylglyoxime with its fewer carbons can participate more in interaction with the solvent than nickel nioxime. Thus, it may be true that the two compounds have nearly the same crystal energies; but less solvent interaction makes it appear that nickel nioxime has a greater lattice energy.

The complexes of nickel diethylglyoxime and nickel dipropylglyoxime could not be included in this study because their crystal structures have not been determined. The crystal structure of nickel ethylmethylnioxime (24) indicates that the nickel atoms are too far apart to form nickel-nickel bonds. The intrinsic solubility of nickel ethylmethylglyoxime is greater than that of nickel dimethylglyoxime. This is not an unexpected result in view of the fact that nickel ethylmethylglyoxime does not form nickel-nickel bonds.

Figure 5. Relationship between solubility and nickel-nickel bond length for some nickel vic-dioximes



There are other forces which contribute to the stability of the crystal of the nickel(II)-vic-dioxime complexes but it is believed that nickel-nickel bonding is not an insignificant factor.

Spectra of Some Nickel(II)-vic-dioxime Complexes

In Figures 2, 3 and 4, the absorption spectra of colloidal suspensions of several nickel(II)-vic-dioxime complexes are compared with the spectra of their chloroform solutions. In each case one observes that the spectrum of the colloidal suspension is different from that of the chloroforms solution. Banks and Barnum (5) observed the same results when they compared the colloidal suspensions and chloroform solutions of some nickel(II)-vic-dioxime complexes which were known to form nickel-nickel bonds. They suggested that the absorption band in the region 425 μ to 557 μ which was not present in chloroform solution must be due to metal-metal bonds. Because the crystal structure of nickel ethylmethylglyoxime (24) excludes the formation of metal-metal bonds and this same band is observed for the colloidal suspension of nickel ethylmethylglyoxime, this band can not be due to metal-metal bonds unless the crystal structure of nickel ethylmethylglyoxime is in error.

In view of these conflicting results, the fact that nickel diethylglyoxime and nickel dipropylglyoxime have absorption bands in this region does not lead to the

conclusion that nickel-nickel bonds are present in the complexes.

Banks and Barnum (5) also observed the absorption spectrum of single crystals of some nickel(II)-vic-dioxime complexes using plane polarized light. Abnormal dichroism was observed. Maximum absorption occurred when the plane of the polarized light was perpendicular to the plane of the molecules. And the direction of the shift in the maximum with change in metal-metal bond length was the same as for the absorption of light by colloidal suspensions of these compounds.

Some single crystals of nickel ethylmethylglyoxime were observed with a polarizing microscope. The dichroism of the crystals is normal because maximum absorption occurs when the plane of the polarized light is parallel to the plane of the molecules. This is the expected result because there are no nickel-nickel bonds in the complex.

Hooker (29) pointed out that the absorption spectrum of the colloidal suspension is not the same as that of the single crystal. He showed by means of X-ray diffraction photographs that the large crystals of nickel dimethylglyoxime are the same as those obtained in the colloidal suspensions. It was pointed out by Banks and Barnum that the difference in the spectrum of the single crystals and the colloidal solution may be due to the fact that in the colloidal solution the

crystals are oriented in all possible directions while when viewed under a polarizing microscope the crystals are always oriented with the needle axis perpendicular to the light beam.

Until the difference between the spectrum of the single crystals and the spectrum of the colloidal suspensions can be explained satisfactorily, the new absorption band in the visible region cannot be unequivocally assigned to the presence of metal-metal bonds.

Heats of Solution

The reason for the selectivity of dimethylglyoxime for nickel(II) has been suggested to be the result of a solubility effect because copper(II) dimethylglyoxime has a larger stability constant than nickel(II) dimethylglyoxime (18). In the crystal of nickel dimethylglyoxime the nickel atoms are arranged in a chain which are believed to be close enough to form nickel-nickel bonds of 3.233 Å. (26). Frasson, et al. (23) report that the organic part of the molecule in copper dimethylglyoxime is interposed between copper atoms of adjacent layers. Furthermore, the copper forms a bond with an oxygen in the adjacent layer. Thus, the copper has a coordination number of five. Dyrssen and Hennichs (20) and also Fleischer (22) studied the solubility of nickel dimethylglyoxime and copper dimethylglyoxime. Dyrssen and Hennichs concluded that the difference in solubility of the two complexes in water is because the copper in the complex has

a tendency to react with the water and acquire a coordination number of five while the nickel in the complex does not become solvated. The heats of solution of the two complexes were determined in water and some organic solvents by Fleischer. Because the heat of solution is a measure of the crystal energy and the energy of solvation, it was necessary to find an inert solvent in which the solvation energies of the two complexes are equal. Fleischer concludes that in benzene and n-heptane the solvation energies of the two complexes are very nearly equal and that copper dimethylglyoxime is more stable than nickel dimethylglyoxime by 2 or 3 kcal. He suggests that the nickel-nickel bond in nickel dimethylglyoxime must be very weak.

One can interpret Fleischer's results differently and reach a different conclusion. For nickel dimethylglyoxime to dissolve in water the nickel-nickel bonds must be broken. This requires energy which will not be returned by solvation of the nickel. When copper dimethylglyoxime dissolves, the copper oxygen bonds must be broken. This requires energy which will be returned when the copper is solvated by the water. But in a non-solvating solvent the solution process involves breaking of nickel-nickel bonds and copper-oxygen bonds for the respective complexes. Clearly then, the difference in their heats of solution will not be an indication that the nickel-nickel bond is extremely weak. This

would indicate that the nickel-nickel bond has about the same strength as the copper-oxygen bond.

In order to get an indication of the significance of the nickel-nickel bond, the heat of solution of nickel dimethylglyoxime and nickel ethylmethylglyoxime were compared in the same solvents which Fleischer used and also in carbon tetrachloride. Nickel ethylmethylglyoxime, according to Frasson and Panatoni (24), does not form nickel-nickel bonds. The results are in Table 16. These results indicate that the solvation energies of the two complexes in n-heptane and carbon tetrachloride are very nearly equal and that the difference in their heats of solution in these solvents represents the difference in their crystal energies. In n-heptane, nickel dimethylglyoxime is more stable than nickel ethylmethylglyoxime by 9.3 kcal and in carbon tetrachloride by 11.3 kcal. Experimental error can account for the difference between these two values. Thus it appears that the nickel-nickel bond contributes about 10 kcal to the stability of the crystal of nickel dimethylglyoxime.

The reason for the small difference in heat of solution between the complexes in benzene can be explained by unequal solvent interaction. Benzene reacts more with nickel dimethylglyoxime than with nickel ethylmethylglyoxime. This less interaction of benzene with nickel ethylmethylglyoxime can be attributed to a shape factor. The ethyl group, which

is not planar with the molecule sterically hinders the interaction.

The entropy changes for the solution process indicate that water reacts quite appreciably with both complexes. The same is true for the chloroform solutions. Water and chloroform both being polar molecules may act in such a way that the vander Waal's atmosphere exerted on the dissolved solutes impedes the free movement of the species in the solution.

Although this method for determining the differences in crystal energies of compounds is idealized, it is believed that this difference of about 10 kcal in their heats of solution in n-heptane and in carbon tetrachloride does approximate the difference in their crystal energies.

SUMMARY

The stability constants of some nickel(II)-vic-dioxime complexes have been measured and compared. It was found that the stability constant for the nickel complexes with the aliphatic ligands did not change appreciably. The same was found to be true for the nickel complexes with the alicyclic series. Because the bonding of the hydrogen in the ligand is different from the bonding of the metal in the complex, a decrease in acid dissociation constant would not necessarily lead to a larger stability constant. The spread in values of the stepwise stability constants was observed to be small.

The increase in the stability constants of the nickel(II)-vic-dioxime complexes in aqueous-dioxane as compared to water solution may be attributed to a decrease in the dielectric constant of the medium. The decrease in the ionizing ability of the medium results in a decrease in the acidic dissociation constant of the vic-dioximes. An increase in the dioxane content of the medium results in increased association of the nickel(II)-vic-dioxime complexes.

Excluding nickel dimethylglyoxime and 4-methylnoxime, a smooth curve resulted from a plot of intrinsic solubility versus nickel-nickel bond length. It could not be explained why nickel 4-methylnoxime is not on the curve. The failure of nickel dimethylglyoxime to fall on the curve could be due to solvent interaction which could be expected to increase

its solubility.

A new absorption band is observed in the visible region of colloidal suspensions of the nickel complexes of ethylmethylglyoxime, diethylglyoxime and dipropylglyoxime. This new band in the absorption spectra of nickel(II)-vic-dioxime complexes has been attributed to metal-metal bonding (5). However, nickel ethylmethylglyoxime does not form metal-metal bonds according to Frasson and Panatoni (24).

The heats of solution of the nickel complexes of dimethylglyoxime and ethylmethylglyoxime were compared in water, chloroform, benzene, heptane, and carbon tetrachloride. It is believed that the energy of solvation for the two complexes are about equal in heptane and carbon tetrachloride. Therefore, the difference in their heats of solution in these solvents represents the difference in their crystal energies. The conclusion is reached that the nickel-nickel bond in nickel dimethylglyoxime has a maximum strength of about 10 kcal.

SUGGESTIONS FOR FUTURE WORK

1. The crystal structure of nickel diethylglyoxime and nickel dipropylglyoxime should be determined in order to find out if nickel-nickel bonds are present in the crystal.

2. The heats of solution of some nickel(II)-vic-dioxime complexes which form Ni-Ni bonds should be determined in n-heptane and carbon tetrachloride. These heats of solution could be compared with that of nickel dimethylglyoxime to see if there is a relationship between crystal energy and metal-metal bond length.

3. A study should be made in order to find out why the absorption spectra of single crystals are different from that of the colloidal suspensions. Orientation of the particle may be an important factor.

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