1972

Transition-Metal Complexes of Beta-Furfuraldoxime.

Max Earl Pickerill
Louisiana State University and Agricultural & Mechanical College

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A Dissertation

Submitted to the Graduate Faculty of the
Louisiana State University and
Agricultural and Mechanical College
in partial fulfillment of the
requirements for the degree of
Doctor of Philosophy

in

The Department of Chemistry

by

Max Earl Pickerill
B.S., Kansas State College at Pittsburg, 1951
M.S., Fort Hays Kansas State College, 1953
December, 1972
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Eddie, Natalie, David, Beverly,

Cindy and Jon
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<td>m.p.</td>
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<td>n.m.r.</td>
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<td>p.p.m.</td>
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<td>aromatic solvent induced shift</td>
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<td>incomplete neglect differential overlap</td>
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<td>DH₂</td>
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ABSTRACT

The ligand, 2-furfuraldoxime, forms air stable crystalline complexes with the bi- and trivalent transitional metal chlorides from chromium to zinc. These compounds have not previously been characterized. They have the general formula

\[ M(\text{FDH})_x \text{Cl}_x \]

in which \( x \) is 2 or 3 depending upon the charge on the central metal cation.

Analytical and spectral data indicate that the metal is six coordinate in these compounds. Electronic spectra support the octahedral configuration. Assignments for the electronic spectra are suggested.

Conductance data indicate that these compounds are non-electrolytes.

All compounds have magnetic moment values typical of high-spin complexes.

Tentative band assignments are suggested for the \( \text{C=N} \) and \( \text{N-O} \) stretching frequencies in these complexes.

The significant displacement of \( \nu(\text{O-H}) \) band and the insignificant (\( \sim 5 \) to \( 10 \text{ cm}^{-1} \)) shift of the \( \nu(\text{O=N}) \) and \( \nu(\text{N-O}) \) bands in the complexes with respect to the free ligand strongly suggest coordination through the oxygen atom of the oxime function.
The infrared hydroxyl band intensity and band width indicate that hydrogen bonding in the tris complexes is much stronger than that in the bis complexes, and framework models suggest the oximino proton is hydrogen bonded to the \( \pi \) electronic system of the furan ring.
INTRODUCTION

Dioximes, as well as monoximes that contain other donor atoms appropriately located in the same molecule, function as bidentate ligands. These compounds have been useful as chelating agents for some time; among those most well-known is DMG, the nickel precipitant. However, since Tschugaeff first reported the formation of \( \text{Ni(DMG)}_2 \), there has been considerable controversy about the structure of these complexes, the manner in which these ligands function, and the mechanism of complexation. This study was an attempt to clarify these questions and to gain some better understanding of these problems. At first glance, \( \beta \)-furfuraldoxime is a ligand which can serve as a bidentate ligand in both syn- and anti stereoisomeric forms.

Elemental analysis, magnetic susceptibilities, conductivities, infrared and electronic spectroscopic data were used to characterize and elucidate these problems. The total information obtained from these methods in conjunction with a comparison of properties of related compounds gives one a perspective view that enables him to correlate structure with the properties of the complexes considered in this study.

Since the theories of conductance, magnetic susceptibilities, and infrared, visible and ultraviolet spectroscopy are well-known, established, and available in many standard textbooks, this author will not expound upon these theories in this dissertation.
CHAPTER I
THEORY

A. Inorganic Complex Compounds.

Inorganic complex compounds consist of a central atom around which are grouped or coordinated a number of ligands. According to Werner, this coordination takes place due to the operation of the auxiliary valence of the central atom. These complexes may be classified on the basis of the Werner system into three main types: addition compounds, penetration compounds and inner complex compounds (1). This classification is actually more formal than intrinsic. Addition compounds are nonionogenic; the bonds between the central atom and the relatively electronegative surrounding atoms are not broken but instead frequently become more stabilized by the entrance of further ligands. Examples of addition compounds are \( \text{Crpy}_3\text{Cl}_3 \) and \( \text{BF}_3\text{NH}_3 \). In a penetration compound the ligands enter between the anion constituent and the cation constituent which functions as the central atom. Examples are \( [\text{Cu(NH}_3)_4]^{2+} \), \( [\text{Co(NH}_3)_6]^{3+} \), \( [\text{Ag(NH}_3)_2]^+ \), and \( [\text{Fe(CN)}_6]^{3-} \). An inner complex compound, by definition, has a metal atom which is bound to an anionic species as well as to a neutral atom in a different position of the same ligand molecule. The resulting inner complex is frequently neutral, but may also be cationic or anionic. Examples are \( [\text{Cugly}_2] \), \( [\text{Siacac}_3]^+ \), and \( [\text{Coacac}_3]^- \).
Metal compounds, in which the metal atom is a member of a ring, are known as chelate compounds. Consequently, a chelating ligand molecule contains more than one site to which the central atom is bonded. The ligands are called bidentate, tridentate, etc., depending on the number of bonded sites in the ligand. Typical examples of chelate compounds are [Coen$_3$]$^{2+}$, [Cutren]$^{2+}$, and ethylenediamine bisacetylacetonecopper(II). The latter structure is given by

\[
\begin{align*}
\text{H}_3\text{C} & \quad \text{O} & \quad \text{Cu} & \quad \text{O} & \quad \text{C} & \quad \text{CH}_3 \\
\text{H-C} & \quad \text{C} & \quad \text{N} & \quad \text{CH} & \quad \text{N} & \quad \text{C} \\
\text{CH}_3 & \quad \text{CH}_2 & \quad \text{CH}_2 & \quad \text{CH}_3
\end{align*}
\]

Therefore, an inner complex salt is a definite type of a chelate compound.

Werner also introduced the concepts of primary and auxiliary valence. The primary valence refers to the charge on the central atom, and the auxiliary valence corresponds to the coordination number which is determined essentially by the electron configuration of the metal atom, and the geometry of the coulombic environment imposed by the neighboring ligand. Since the charge of the metal atom is satisfied through the anion of the ligand, inner complex salts are frequently non-electrolytes. The saturation of the combining power of the central atom by more than one atom of the same
molecule results in ring formation and tends to inhibit the
dissociation of the complex and/or addition of solvent molecules by
ligand displacement. Decreased hydration tendencies result in lower
water solubilities. The covalent character of inner complex salts
is indicated by water insolubility, by solubility in organic liquids,
and by the fact that the products often can be sublimed or distilled
without decomposition. The inner complex salts of transitional metal
ions are frequently colored, or a deepening in color may often
accompany their formation from less colored components. This color
change is often significant in analytical determinations. Examples
are:

\[
\begin{align*}
\text{Fe}^{2+} & \rightarrow [\text{Fe o-phenan}_3]^{2+} \\
(\text{light green}) & \rightarrow (\text{deep red})
\end{align*}
\]

\[
\begin{align*}
\text{Co}^{3+} & \rightarrow [\text{Co-oxo-nitroso-β-naph}_3] \\
(\text{red}) & \rightarrow (\text{deep red})
\end{align*}
\]

\[
\begin{align*}
\text{Ni}^{2+} & \rightarrow [\text{NiEMG}_2] \\
(\text{light green}) & \rightarrow (\text{deep red})
\end{align*}
\]

The production of inner complex ring systems depends not
only on the nature of the central atom but also on the necessity for
the complex-forming groups to be in a geometry favorable for ring
closure.

In the foregoing sections, we deliberately cited examples to
demonstrate that complex formation, that is defined by the opening
sentence, is not limited to transitional metals; nevertheless, the
exhaustive study of the complexes of transitional metals has led to a large extent to the present understanding of coordination chemistry.

B. Oximes.

An oxime may be regarded to be the product of a carbonyl condensation with hydroxylamine. The oximes contain the group \( \text{C}=\text{NOH} \). The word oxime is a contraction of oxy-imine and was introduced by Meyer (2). Some oximes are considered to be isonitroso compounds because they are isomers of primary or secondary nitroso compounds that have the respective formulas, \( \text{RCH}_2\text{N}=\text{O} \) and \( \text{R}_2\text{CH-N}=\text{O} \).

C. Oxime Preparations.

There are two general methods for the preparation of an oxime. The first method is the reaction of hydroxylamine with an aldehyde or ketone to give an aldoxime or a ketoxime respectively. This general reaction is represented by the equation

\[
\begin{align*}
\text{R}' & \quad \text{R} \quad \text{C}=\text{O} + \text{H}_2\text{NOH} \rightarrow \text{R}' & \quad \text{R} \quad \text{C}=\text{NOH} + \text{H}_2\text{O} \\
(\text{H}) & \quad (\text{H})
\end{align*}
\]

The products of this reaction are usually sharp-melting, crystalline solids which are derivatives of aldehydes and ketones that are often prepared for identification and characterization of the parent carbonyl compound. Aldehydes usually react more readily than ketones, and aliphatic ketones are more reactive than aromatic ketones.
Aliphatic ketoximes or aldoximes are usually prepared by simply mixing the carbonyl compound with an equivalent of hydroxylamine in water and separating the product by an ether extraction. In some cases it is necessary to add an excess of alkali. In the case of an aromatic ketoxime preparation, it is usually necessary to reflux an ethanolic solution of the ketone, an equivalent of hydroxylamine hydrochloride, and excess sodium acetate.

The rate of oxime formation depends on the hydrogen ion concentration of the reaction mixture. It has been shown that the ketoxime formation between acetone and hydroxylamine is bimolecular and reversible; the rate of formation of the ketoxime and the hydrolysis of the ketoxime are dependent on the pH of the solution. The rate of formation of acetoxime is greatest at pH 4.7; whereas the rate of hydrolysis of the oxime is greatest at pH 2.3 but is least above pH 5 (3). The usual procedure for preparation of the ketoxime requires the use of a solution containing a mixture of acetic acid and sodium acetate to buffer the solution to a pH of approximately five.

Since hydroxylamine is weakly acidic and can be converted to a more reactive nucleophile by loss of a proton, oxime formation is preferably base-catalyzed. B represents a Lewis base in the following equations that summarize a mechanism for the oxime formation.

\[
\text{NH}_2\text{OH} + :B \rightarrow BH^+ + :\text{NH}_2\text{O}^- \rightarrow :\text{NHOH} + BH^+ \\
R_2\text{C}=\text{O} + \text{NHOH} \rightarrow R_2\text{C}=-\text{OH} \rightarrow R_2\text{C}=\text{NOH} + \text{OH}^-
\]
The best-known dioximes are those prepared from 1,2-diketones and alpha-ketoaldehydes. Dimethylglyoxime, which is used to precipitate nickel and palladium quantitatively, is an example of a dioxime. The 1,2-diketones readily form the monoxime, but more vigorous conditions are required to obtain the dioxime.

The 1,3-diketones normally do not form oximes as final products, but they are converted to an isoxazole by loss of two molecules of water. The reaction follows.

\[
\text{R-C-CH}_2\text{-C-R' + H}_2\text{NOH} \rightarrow \text{R-C-CH}_2\text{-C-R' + H}_2\text{O} \rightarrow \text{R-C-C-H} + 2\text{H}_2\text{O}. 
\]

The second general method for the preparation of an oxime is the reaction of nitrous acid or one of its esters with a compound containing a reactive methyl or methylene group.

\[
\text{R-C-CH}_2\text{-R' + HON=O} \rightarrow \text{R-C-C-} + \text{H}_2\text{O}. 
\]

Victor Meyer and J. Zublin in 1878 obtained the first known oxime, oximino-acetone, by this method (4).

The enolic form of the ketone seems to be the form which reacts, and ketones which are not 1,3-diketones do not react readily with nitrous acid. The alternate procedure involves the catalyzed reactions of the ketone with an ester of nitrous acid. Sodium ethoxide
is the usual catalyst, and freshly prepared pentyl nitrite is a useful ester of nitrous acid.

D. Stereoisomerism.

One of the most interesting features in oxime chemistry is stereoisomerism which is the classical example of geometrical isomerism in nitrogen compounds. The stereochemistry is considered extensively because stereoisomerism of the oxime is intimately involved with the geometry of the complex, the ligation site, and the spectral and other characteristics of the complex.

Early work in this area resulted in the isolation of two forms of the dioxime of benzil by Goldschmidt; a third form of the same compound was discovered by von Auwers and Meyer in 1889. These three species, the so-called α, β, and γ forms, though similar in some chemical respects, differ markedly in some reactions. For example, the α-dioxime forms a complex with nickel that has the formula NiR₂; the β-dioxime does not form a nickel complex; and the γ-dioxime forms a complex that has the formula NiR. The R represents the ligand of the dioxime after the loss of one hydrogen atom. It is interesting to note that the alpha and gamma dioximes can be converted into the β-dioxime by heating them in ethanolic solutions.

An explanation of reactivity differences in terms of isomerism was offered by Hantzsch and Werner in 1890 (5). Cases of geometrical isomerism had been recognized by van't Hoff to be a consequence of restricted rotation about double bonds that results in cis-trans isomers. Hantzsch and Werner simply extended van't Hoff's
concept to the oximes by postulating that there is restricted rotation about the carbon to nitrogen double bond and that the terminal bond on the nitrogen in the planar $\text{C=N}$ is not colinear with the $\text{C=N}$ bond. With the exception of formaldehyde, the oxime of an aldehyde or unsymmetrical ketone should exhibit geometrical isomerism of the type:

\[
\begin{align*}
\mathrm{(I)} & \quad R \quad \mathrm{C} \quad R' \\
\mathrm{N} \quad \mathrm{OH} \\
\end{align*}
\]

\[
\begin{align*}
\mathrm{(II)} & \quad R \quad \mathrm{C} \quad R' \\
\mathrm{OH} \quad \mathrm{N} \\
\end{align*}
\]  

\[R' \neq R \text{ or } R' = H\]

The three benzildioximes mentioned previously may exist in three, and only three, forms; these forms are shown below and are examples of the expected isomers.

\[
\begin{align*}
\mathrm{(III)} & \quad \mathrm{Ph-C} \quad \mathrm{C-Ph} \quad \mathrm{HON} \quad \mathrm{NOH} \\
\mathrm{(IV)} & \quad \mathrm{Ph-C} \quad \mathrm{C-Ph} \quad \mathrm{NOH} \quad \mathrm{N OH} \\
\mathrm{(V)} & \quad \mathrm{Ph-C} \quad \mathrm{C-Ph} \quad \mathrm{NOH} \quad \mathrm{NOH} \\
\end{align*}
\]

Compound (III) is the $\alpha$-dioxime, compound (IV) is the $\beta$-dioxime, and compound (V) is the $\gamma$-dioxime or the amphi form.

A convincing argument in support of the Hantzsch and Werner view is based upon the products formed when stereoisomeric oximes undergo the Beckmann rearrangement. In the Beckmann rearrangement
a ketoxime is treated with phosphorus pentachloride or certain acidic reagents, and the product is hydrolyzed to yield a substituted amide. This reaction may be represented by the reaction scheme

\[
R' \begin{array}{c} \text{C}=\text{OH} \\ \text{R} \end{array} \rightarrow \begin{array}{c} \text{HO} \\ \text{R} \end{array} \begin{array}{c} \text{C}=\text{NR} \\ \text{R} \end{array} \rightarrow \begin{array}{c} \text{O} \\ \text{R} \end{array} \begin{array}{c} \text{C}=\text{NHR} \\ \text{R} \end{array}.
\]

Thus, in the case of two isomeric ketoximes there are two main products that are dependent on whether the R or the R' group migrates and exchanges position with the OH group. In the Beckmann rearrangement the group that migrates is trans with respect to the OH group, and the two possible main products from two isomeric ketoximes are the amides that have the formula of R-CONHR' and R'-CO-NHR. This rearrangement is strong support for the argument that the two isomeric oximes have structures of the same functional type but differ from one another stereochemically.

When Hantszch and Werner proposed their explanation of isomerism, they also suggested methods for the determination of configuration of both aldoximes and ketoximes. They were the first persons who pointed out the difference in the reaction of the two isomeric acetyl derivatives of aldoximes with aqueous sodium carbonate; one isomer is hydrolyzed to the oxime, and the other isomer loses acetic acid to give a nitrile. If it is assumed that nitrile formation occurs because the hydrogen atom and the acetyl group are on the same side of the double bond, then the reactions of the two isomeric aldoximes should be those that are indicated below.
They gave the name syn-aldoxime to the aldoximes that have the hydrogen atom attached to carbon and the hydroxyl group attached to nitrogen on the same side of the double bond and the name anti-aldoxime to those that have the other configuration.

The assumptions of Hantzsch and Werner about the reactions of the two isomeric aldoximes with aqueous sodium carbonate have proved to be erroneous, but this reaction still remains the crucial test for the determination of configuration of oximes. Modern methods of structure determination show that the loss of acetic acid involves the trans group and not the cis group that was assumed by Hantzsch and Werner. The proper identification of the aldoximes now has the hydrogen atom and the hydroxyl atom on the same side of the double bond in the case of the $\alpha$-aldoxime and the hydrogen atom and the hydroxyl group on the opposite side of the double bond in the case of the $\beta$-aldoxime. These orientations are represented below.
A more recent advance in stereochemical nomenclature is the E-Z system (8). According to the Cahn-Ingold-Prelog (R-S) system, a precedence had been established for the groups. For the molecule, UXC=CYZ, assume that the mass preferences, U > X and Y > Z follow from the C-I-P system. Then the two possible isomers are named in the following manner.

Thus, Z (from the German zusammen) implies that the groups of higher precedence are on the same side of the two carbons of the double bond; whereas, the symbol E (from the German entgegen) means that the precedence atoms are across the double bond from each other.

In summary, the prefixes trans, anti, β or Z when applied to 2-furfuraldoxime should be associated with the following configuration (VIII):
Whereas, the prefixes cis, syn, α, or E imply the following configuration (IX):

\[ \text{(IX)} \]

One of the methods used to establish configuration assignment is the result of ring-closure. Brady and Bishop (6) in 1925 demonstrated that the β-oxime of 2-chloro-5-nitrobenzaldehyde loses hydrogen chloride readily with an alkali, but the α-oxime does not lose hydrogen chloride readily. The cyclic compound, indoxazene, which is an intermediate from the β-oxime reaction then forms nitrosalicyclic nitrile as the final product. Therefore, the β-oxime must have the configuration shown above in structure (VII), and since its acetyl derivative loses acetic acid and is not hydrolyzed to the oxime, the converse of Hantzsch's assumption must be true. As a consequence the literature of the years 1887 to 1925 is erroneous in the assignment of configuration for isomeric aldoximes. The assigned configuration of syn-p-chlorobenzaldoxime has been confirmed by the results of x-ray crystal analysis (7).
Only rarely can the oximes be obtained in the two geometrically isomeric forms. Examples of aldoximes known in two forms are the substituted benzaldoximes and the oximes of furfural and cinnamaldehyde.

The configuration of an aldoxime which exists in only one form can be established by chemical methods. In general, there is a marked difference between the two isomers in the reaction of the acetyl derivatives with alkali carbonate. The oxime regenerated from its acetyl derivative by alkali carbonate is called the α-oxime and the other oxime not regenerated from its acetyl derivative is the β-oxime. β-oximes can be transformed into the isomeric α-oximes quite easily; the reverse change can be effected by hydrochloric acid, sulphuric acid, and often by the action of ultraviolet light. The β-aldoximes usually form metallic derivatives with transitional metal salts such as those of copper and iron; the α-oximes seem, in general, not to form the corresponding derivatives, but with a metallic salt give the metallic derivative of the β-oxime.

Most aldoximes exist as equilibrium mixtures of both forms, and the equilibrium ratio may be determined by means of nmr spectra. For example, the acetaldoxime ratio of syn/anti is 0.64 at 25°C (9).

The interconversion of isomeric oximes can be accomplished in various ways. Heating the oxime in solution lends to convert the less stable isomeric oxime into the more stable form. In the case of the benzil monoximes, in which the α-oxime is the less stable, the rate of change of isomerism can be measured because only the α-oxime reacts with copper acetate to give an oxime-copper complex, and this
fact can be applied to the analysis of a mixture of the α- and β-oximes (10, 11). In alcoholic solution, HCl is an effective equilibration catalyst. More surprisingly, salts such as LiCl are more efficient catalysts than HCl at the same concentration. The rates of stereoisomeric change are not proportional to the concentration of the salt but increase rapidly at the higher concentrations. These facts seem to indicate that the actual catalyst is the undissociated molecule (associated ion-pair) of the catalyst, which has an appreciable concentration only in the more concentrated solutions. It seems that upon the close approach of an ion-pair and a molecule of the α-oxime there is an interaction between the field of the ion-pair and the C=N system, which causes a decrease in the torsional rigidity of the double bond so that the α-oxime can change easily into the more stable β-oxime.

It has been shown by Taylor (12) that the presence of catalysts such as the chloride ion or active charcoal often effects the interconversion of the isomeric oximes, but this interconversion is not observed in the case of their O-methyl ethers. If the charcoal is heated in hydrogen to remove the surface oxygen, the effect disappears. The catalyst is the active oxygen adsorbed on the surface of the charcoal, and the mechanism of the catalysis is an exchange of oxygen atoms. If an active oxygen atom on the charcoal becomes attached to the nitrogen of the oxime group, it can become attached only on the side of the double bond opposite to that of the hydroxyl group already present. The hydrogen atom of the hydroxyl group can migrate to this new oxygen atom, and the oxime
molecule can then leave the surface in the more stable $\beta$-configuration and leave behind the original oxygen atom of the oxime group. This explanation accounts for the absence of the phenomenon in the $\theta$-ethers because the migration of a methyl group is considerably less favorable than the migration of an hydrogen atom.

Bryson and Dwyer (23) have shown that $\alpha$-furfuraldoxime is easily transformed to the $\beta$-isomer by rearrangement in the presence of metallic salts.

E. Transitional Metal Complexes with Oximes.

In general, the nitrogen atom of an oxime ($-\text{NOH}$) group serves as a good donor atom. As an illustration, dimethylglyoxime forms the analytically valuable, insoluble red inner complex salt with nickel and a yellow complex with palladium. The structure of the insoluble red nickel salt proposed by Pfeiffer (13, 14) is

The nickel, in this structure (X), is directly bound to the nitrogen atoms of both oxime groups; it is bound to one nitrogen by a principal valence and to the other nitrogen by an auxiliary valence to form a five-membered ring. A similar ring is present in the salts of
2-pyridylphenylketoxime and 2-pyridylmethylketoxime. This ring is shown by their coordination formulas:

\[ \begin{align*}
&\text{XI} \\
\end{align*} \]

The Tschugaeff reagent, dimethylglyoxime, is the best known nickel precipitant. Ponzio has shown that numerous other \( \alpha \)-dioximes also react with nickel salts to form colored precipitates. These chelates are inner complex compounds, and the structure of \( \text{Ni(DMG)}_2 \) has been established by x-ray methods to be

\[ \begin{align*}
&\text{XIII} \\
R = \text{CH}_3
\end{align*} \]

Meisenheimer proved that the \( \alpha \)-dioximes have the anti configuration (XIV).
Since the two hydroxyl groups in anti configuration (XIV) are relatively remote, the formation of an inner complex salt involving the hydroxyl groups seems unlikely. Pfeiffer (13,14), however, proposed and proved a five-membered chelate ring in which the metal was directly bound to the two nitrogen atoms (XV). According to this concept, the syn dioximes are incapable of salt-formation, and the amphi dioximes form a different type of nickel salt. The difference in reactivity of the α-dioximes with nickel salts is explained by the stereochemistry of the oxime groups that is shown by the following structures.

Brady and Muers (15) offered further support for the Pfeiffer formulation of the nickel-dioxime salts by showing that the hydroxyl group of the second oxime group is not directly involved in the formation of the complex salt of the O-methyl ether of dimethyl-glyoxime that has the following structure (XVIII):
The -C(\textit{NOH})-C(\textit{NOH})- group's chelating ability is influenced by the remainder of the molecule. For example the dioximes of the aromatic orthoquinones have lesser selectivity than do the simple dioximes, and 1,2-naphthoquinone acts as a dibasic acid to form precipitates with almost all metals. The aromatic ring influence seems to destroy the nickel-binding action of the two oxime groups, but this action is restored if the aromatic ring character is removed by hydrogenation to give the compound 1,2-cyclohexanedionedioxide (XIX)

This compound is the cyclic analogue of dimethylglyoxime, and Wallach (16) has shown that its nickel compound is similar to nickel dimethylglyoximate.

Feigl states that the sensitivity of the nickel test with cyclohexanedioxime is twice as great as that with dimethylglyoxime.
The cyclohexanedioxime is water soluble in contrast with the dimethylglyoxime reagent which must be used in alcoholic solution. Soule (17) has also shown that α-furildioxime (XX)

\[
\begin{align*}
\text{N} & \quad \text{I} \\
\text{HON} & \quad \text{NOH}
\end{align*}
\]

(XX)

is soluble in hot water and may be used as a reagent for the analytical determination of nickel.

According to Pfeiffer, the essence of the nickel-binding groups is the bonding of nickel by one auxiliary and one principal valence to two nitrogen atoms to form a five-membered ring. The nickel-binding action is not limited, therefore, to the dioximes; other compounds that form characteristic inner complex nickel salts are 2-pyridylmethylketoxime, (XXI) and 2-pyridylphenylketoxime (XXII). These inner complex nickel salts are

\[
\begin{align*}
\text{N} & \quad \text{I} \\
\text{HON} & \quad \text{NOH} \\
\text{Ni} & \quad 2
\end{align*}
\]

(XXI)

\[
\begin{align*}
\text{N} & \quad \text{I} \\
\text{HON} & \quad \text{NOH} \\
\text{Ni} & \quad 2
\end{align*}
\]

(XXII)
Supposedly, a lone oxime group does not coordinate firmly, but when it forms part of a chelate ring, the dioxime nitrogen has strong donor properties, and these oximes are useful in inorganic analysis. Dimethylglyoxime may be considered to be a specific reagent for nickel and palladium, but the specificity depends upon the reaction conditions. Nickel is precipitated from ammoniacal solutions; whereas palladium precipitates only from weak mineral acid solutions. The specificity for nickel and palladium is, therefore, pH dependent.

Tschugaeff (18, 19) has shown that metallic ions having a coordination number of six combine with only two dioxime groups while the remaining positions are filled by other donors such as ammonia or halogens.

Ablov (20) prepared dimethylglyoxime-cobalt compounds of the type \([\text{Co(HD)}_2(\text{NH}_3)_2]X\), \([\text{Co(HD)}_2(\text{NH}_3)X]\), and \([\text{Co(HD)}_2X_2]\) in which the ammonia molecules are replaced by aniline or an aniline derivative.

F. Furfuraldoxime as a Chelate Group.

\(\beta\)-furfuraldoxime, \(\text{C}_9\text{H}_5\text{NO}_2\), crystallizes from ligroin as a white needle-like solid that has a melting point of 91-92° and a decomposition temperature of 201-208° (21). It is partially soluble in water and very soluble in alcohols, ether, benzene, carbon disulfide and acetic acid.

\(\alpha\)-furfuraldoxime, \(\text{C}_9\text{H}_5\text{NO}_2\), is a white crystalline solid that has a melting point 74-75° and is moderately soluble in water and extremely soluble in alcohol and acetone.
The configurations of the two isomeric aldoximes were confirmed by Brady (22), who demonstrated that treatment with acetic anhydride gave the acetyl derivative in the case of the syn configurations and the nitrile derivative in the case of the anti form.

Since the oxygen of the furan ring has a lone electron pair in addition to the oxygen electrons involved in the aromatic delocalization, it should serve as a donor atom to form a coordination compound with metallic salts. The planar five-membered ring of furan containing six $\pi$-electrons exhibits the strong aromatic character that is expected of such a system. The filled orbital on the oxygen atom containing the unshared pair overlaps with the adjacent $p$-orbitals to create the aromatic sextet of $\beta$-furfuraldoxime. The aromaticity of the furan ring may be represented by canonical forms such as:

Indeed, the heat of hydrogenation is only 36.6 kcal/mole for furan as compared with 53.8 kcal for two moles of cyclopentene. The difference of 17.2 kcal is the resonance energy of the furan ring system (25, 26). The fact that the oxygen of the furan ring should serve as a donor atom to form a coordination compound with metallic salts was experimentally tested by Bryson and Dwyer (27) in their preparation of a number of addition compounds with metallic salts.
Their results indicated that the alpha oxime did not yield addition compounds with metallic salts but instead rearranged under the influence of the metal to give an addition compound of the $\beta$-oxime. This reaction also seems to follow the general pattern for syn aromatic oximes (28).

Palladium alone of all the common metals forms complexes with $\alpha$-furfuraldoxime (29). $\alpha$-benzilmonoxime (XXIII) (according to older literature) may be considered analogous to $\alpha$-furfuraldoxime (XXIV) in structure and displays dissimilar donor properties as a ligand.

\[
\begin{align*}
\text{(XXIII)} & \quad \text{(XXIV)} \\
\end{align*}
\]

One would expect complex formation with metals as copper, nickel, cobalt palladium, but palladium seems to be the only metal which forms an inner complex with $\alpha$-furfuraldoxime, whereas $\alpha$-benzilmonoxime form typical inner complexes with the metals mentioned above (13,14).

Hieber and Leutert (28) examined a number of $\beta$-oxime addition complexes with the general formula $\text{MX}_2(\text{C}_5\text{H}_5\text{O}_2\text{N})_4$ in which the metal oxime link seemed to be through the nitrogen of the oxime. Thirteen years later, Bryson and Dwyer (29) proposed that $\beta$-furfuraldoxime can yield internal complex metallic salts through coordination with the oxygen of the furan ring.
Although \( \beta \)-fururaldoxime does form inner complex derivatives with many metals; there appears, however, to be some resistance to the formation of compounds with the oxygen to metal link. In some cases the orthodox nitrogen to metal link tends to be achieved by the formation of binuclear complexes that often contain three oxime groups or of complexes that have four oxime groups associated with the central bivalent metal.

Since \( \beta \)-fururaldoxime has the anti structure, steric considerations preclude the formation of the usual monomeric chelated metallic derivatives in which the metal is always joined to the nitrogen of the oxime group, and the bonding must be metal to oxygen. The bonding postulated by Bryson and Dwyer is represented by structure (XXVI)

![Structure (XXVI)](image)

G. **Hydrogen Bonding.**

In a solution the hydrogen bonding species present depend on the concentration, temperature, and the nature of the solvent and solute. Intermolecular hydrogen bonds, in contrast to intramolecular hydrogen bonds, do not have a spatial requirement and are the result
of molecular association. The intermolecular association effects disappear with dilution whereas the intramolecular hydrogen bonding effect is retained, and the infrared spectral response follows Beer's law. Therefore a comparison of spectra, if measured in the same inert solvent, should experimentally distinguish the extent of intr- and intermolecular hydrogen bonding.

Since individual bonds never vibrate completely independently with respect to the remainder of the molecule, infrared band positions vary according to the nature of the complex. Band position also depends on the experimental conditions because these conditions will affect the geometry and the environment of the molecule.

Pimentel and McClellan (30) state that the O-H stretching mode and its harmonics are shifted to lower frequencies by hydrogen bond formation, and in many systems these shifts are approximately ten percent of the fundamental. According to these authors, high values of molar absorptivities are usually observed in the case of intermolecular hydrogen bonded substances in contrast to low values for intramolecular hydrogen bonded species. Sen and Malone (31) reported high molar absorptivities due to intramolecular hydrogen bonding in HPPK and its complexes. Therefore, a high value of molar absorptivities may not be an unequivocal criterion of intermolecular hydrogen bonding.
A. Materials.

The ligand, 2-furfuraldoxime, was purchased from Eastman Organic Chemicals. The isomer was the beta form of the oxime that has a melting point of 90-91°C which corresponds to the literature value for the pure beta or anti-oxime (23). All chemicals used were reagent grade materials; the solvents were purified whenever it was deemed necessary.

B. Preparation of the Compounds.

**Dichloro-bis-(2-furfuraldoxime)nickel (II):**

FDH (4.44 g, 0.04 moles) was dissolved in 100 ml of absolute ethanol and then added dropwise to a hot refluxing mixture of NiCl₂·6H₂O (4.76 g, 0.02 moles) in 100 ml of absolute ethanol. The solution was refluxed for four hours. Yellow-green crystals separated after the solution was cooled. The product was filtered, washed with acetone, washed with normal pentane, and dried under vacuum.

**Dichloro-bis-(2-furfuraldoxime)cobalt (II):**

FDH (4.44 g, 0.04 moles) was dissolved in 80 ml of absolute ethanol and then added dropwise to a hot refluxing mixture
of CoCl₂·6H₂O (4.76 g, 0.02 moles) in 150 ml of absolute ethanol. The mixture was distilled to remove the excess ethanol and a tan-colored solid separated from the dark blue solution. The solid was filtered, washed with normal pentane, and dried under vacuum.

**Dichloro-bis-(2-furfuraldoxime)copper (II):**

FDH (4.44 g, 0.04 moles) was dissolved in 100 ml of absolute ethanol and added dropwise to a hot refluxing solution of CuCl₂·2H₂O (3.4 g, 0.02 moles) in 150 ml of absolute ethanol. The green colored solution turned red-brown after addition of the ligand, and light, feathery red-brown crystals formed. The product was filtered, washed with absolute ethanol, and dried under vacuum.

The above procedure was repeated with a one to one mole ratio of the ligand, β-furfuraldoxime and the copper salt with the exception that the mixture was refluxed for two hours, and the excess ethanol was removed by distillation. When approximately one-half of the ethanol was removed, the red-brown feathery crystals formed. Elemental analyses indicated that the one to one mole ratio and the one to two mole ratio of ligand and metal ion yielded the same compound.

**Dichloro-bis-(2-furfuraldoxime)manganese (II):**

FDH (4.44 g, 0.04 moles) was dissolved in 100 ml of absolute ethanol and then added dropwise to a hot refluxing mixture of MnCl₂·4H₂O (2.52 g, 0.02 moles) in 150 ml of absolute ethanol.
A yellow-brown solid separated from the solution after refluxing for two hours. The mixture was distilled to a volume of approximately 75 ml, decanted, and washed with hot cyclohexane in a Gooch filter. Final washing with acetone and vacuum drying left a product that was light tan in color.

**Dichloro-bis-(2-furfuraldoxime)iron (II):**

FDH (4.44 g, 0.04 moles) was dissolved in 80 ml of absolute ethanol and then added dropwise to a hot refluxing solution of FeCl₂·H₂O (3.98 g, 0.02 moles) in 150 ml of absolute ethanol. A nitrogen sweep was used to prevent possible air oxidation of the ferrous to ferric ion. The excess ethanol was removed by distillation to a volume of approximately 50 ml, and a light brown solid precipitated. The product was filtered, washed with absolute ethanol, washed with hot cyclohexane, and dried on the vacuum line.

**Dichloro-bis-(2-furfuraldoxime)zinc (II):**

FDH (4.44 g, 0.04 moles) was dissolved in 100 ml of absolute ethanol and then added dropwise to a refluxing solution of ZnCl₂ (2.72 g, 0.02 moles) in 150 ml of absolute ethanol. The mixture was refluxed for two hours, and the excess ethanol was removed by vacuum distillation. The off-white residue was washed repeatedly with hot cyclohexane to remove the brown color, the liquid was decanted, and the product was dried on the vacuum line.
Trichloro-tris-(2-furfuraldoxime)iron (III):

FDH (6.66 g, 0.06 moles) was dissolved in 100 ml of absolute ethanol and then added dropwise to a refluxing solution of FeCl$_3$$\cdot$6H$_2$O in 150 ml of absolute ethanol. The light yellow brown solution changed to a dark brown color upon addition of the ligand. The ethanol was removed by vacuum distillation, and the nearly black crystals were washed with hot cyclohexane, decanted, and dried on the vacuum line.

Trichloro-tris-(2-furfuraldoxime)chromium (III):

FDH (3.53 g, 0.03 moles) was dissolved in 100 ml of absolute ethanol and then added dropwise to a refluxing mixture of CrCl$_3$$\cdot$6H$_2$O (2.66 g, 0.01 moles) and 50 ml of absolute ethanol. The deep green alcoholic chromium salt solution turned almost black in color on addition of the ligand. The mixture was reduced to a volume of approximately 20 ml by distillation to remove the excess ethanol, and the remaining 20 ml was removed by vacuum distillation. The dark green crystals were washed with hot cyclohexane, decanted, and dried under vacuum.

C. Spectrophotometric Measurements.

The electronic absorption spectra of nujol mulls of the solid compounds on Whatman 42 filter paper and of solutions in matched silica cells were recorded in the range of 20,000-2,000 Å by means of a Cary 14 Recording Spectrophotometer. The ethanolic
solutions were approximately $10^{-3}$ M based on the formula weight of
the analyzed complex.

Spectrophotometric measurements in the i.r. region were
recorded in the 600-4,000 cm$^{-1}$ region by means of a Beckman IR-10
spectrophotometer. The mull spectra of the complexes were obtained
by the use of hexachlorobutadiene as the mulling agent. Since the
solubility of the solid compounds was extremely low, a reasonable
concentration could not be obtained in a solvent which was non-
absorbing in the region of interest. Consequently, good solution
spectra were not obtained.

D. Magnetic Susceptibility Measurements.

Measurements of the magnetic susceptibility of the metal
chelate compounds of β-furfuraldoxime were obtained by the Gouy
method by means of an Ainsworth type BCT balance and an Alpha
Scientific Lab., Inc. model Al 7500 electromagnet. Since the
measurement of magnetic susceptibilities by the Gouy method is a
relative one, the complex mercury (II) tetrathiocyanocobaltate (II)
was used as the calibrant. This is a popular standard because it
has the following advantages, (1) It is easily prepared and purified;
(2) it has an accurately known moderate susceptibility ($\chi_g \sim 10^{-5}$);
(3) it is stable in moist air; (4) $\chi_g$ varies in a known and simple
way as the temperature changes; (5) it is easily and reproducibly
packable in the Gouy tube (32). A bulk sample was used according to
the method of Angelici (33), and all values were corrected for
diamagnetism of the ligands and the metal ion.

E. **Conductivity Measurements.**

The molar conductance of solutions of the furfuraldoxime compounds were calculated from the measured resistances of $10^{-3}$ to $10^{-4}$ M ethanolic solutions. Resistance measurements were made by use of a Leeds and Northrup model No. 4866 conductivity bridge operating at 60 c.p.s. A cell constant for the conductivity cell was determined by using a standard potassium chloride solution. The cell constant was 10.72 cm$^{-1}$, and the absolute ethanol had a specific conductance of less than $10^{-7}$ ohm$^{-1}$. The conductance of 1 x $10^{-3}$ M sodium iodide in ethanol was determined for use as a reference value for an uni-univalent electrolyte. The reference value for NaI is 35 cm$^2$/ohm mole.

F. **Elemental Analysis.**

Carbon, hydrogen, and nitrogen analyses were performed by Mr. Ralph Seab, microanalyst of this department. Chloride was determined gravimetrically as silver chloride.

All metals were determined gravimetrically according to procedures outlined by Vogel (34); nickel with dimethylglyoxime, cobalt with α-nitroso-β-naphthol, copper with quinaldic acid, and zinc with 8-hydroxyquinoline.
G. Melting Points.

The melting points of all compounds were determined by means of a Thomas-Hoover Capillary Melting Point Apparatus. The decomposition temperature or melting points of the compounds were recorded without correction or thermometer calibration.

H. Molecular Weights.

The molecular weights of all compounds were determined by use of the Beckmann freezing point depression method. The molecular weights of the complexes of iron (III) and chromium (III) prepared from a one to three metal to ligand ratio were determined with the use of nitrobenzene as the solvent. The cryoscopic constant of nitrobenzene is 8.10 degrees/molal. The molecular weights of all other compounds prepared were determined with the use of dimethylsulfoxide as the solvent. A cryoscopic constant of 4.64 degrees/molal was determined for dimethylsulfoxide with the use of naphthalene as the solute.
CHAPTER III
RESULTS AND DISCUSSION

A. Physicochemical Data.

The analytical data are given in Table I, and other pertinent data are given in Table II. The compounds, with the exception of the iron (III) complex, are fairly stable in air. The iron (III) compound slowly undergoes a compositional change which was detectable by the color change to a deep black color after the compound stood at room temperature for several weeks. The compounds are not highly soluble in water nor in common organic solvents such as CCl₄, CHCl₃, C₆H₆, (CH₃)₂CO and EtOH; however they are fairly soluble in DMSO and DMF. The melting point range for the complexes varied from 94° to 225°; half of the eight complexes decomposed at the incongruent melting point.

The analytical and molecular weight data clearly indicate that the ligand combines with the divalent metals in a 1:2 mole ratio of metal to ligand: whereas the trivalent metals combine in a 1:3 mole ratio of metal to ligand. Since the coordination number is six for an octahedral complex, this condition requires the ligand to be bidentate in the metal (II) complexes and requires two chlorides to be coordinated to the metal. In the case of the metal (III) complexes the ligand is monodentate, and three chlorides are directly coordinated to the metal.
TABLE I
ELEMENTAL ANALYSIS OF THE COMPOUNDS*

<table>
<thead>
<tr>
<th>Complex</th>
<th>%N</th>
<th>%C</th>
<th>%H</th>
<th>%Cl</th>
<th>%M</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr(FDH)₃Cl₈</td>
<td>8.55</td>
<td>36.65</td>
<td>3.07</td>
<td>21.57</td>
<td>---</td>
</tr>
<tr>
<td></td>
<td>*8.34</td>
<td>36.65</td>
<td>3.23</td>
<td>20.83</td>
<td>---</td>
</tr>
<tr>
<td>Mn(FDH)₂Cl₂</td>
<td>8.04</td>
<td>34.48</td>
<td>2.87</td>
<td>20.37</td>
<td>---</td>
</tr>
<tr>
<td></td>
<td>*8.02</td>
<td>34.26</td>
<td>2.84</td>
<td>20.37</td>
<td>---</td>
</tr>
<tr>
<td>Fe(FDH)₂Cl₂</td>
<td>8.03</td>
<td>34.48</td>
<td>2.87</td>
<td>20.32</td>
<td>---</td>
</tr>
<tr>
<td></td>
<td>*8.09</td>
<td>33.72</td>
<td>2.95</td>
<td>20.24</td>
<td>---</td>
</tr>
<tr>
<td>Fe(FDH)₃Cl₃</td>
<td>8.49</td>
<td>36.30</td>
<td>3.03</td>
<td>21.40</td>
<td>---</td>
</tr>
<tr>
<td></td>
<td>*7.98</td>
<td>35.58</td>
<td>2.92</td>
<td>20.11</td>
<td>---</td>
</tr>
<tr>
<td>Co(FDH)₂Cl₂</td>
<td>7.96</td>
<td>34.10</td>
<td>2.84</td>
<td>20.14</td>
<td>16.74</td>
</tr>
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<td>2.84</td>
<td>20.01</td>
<td>16.71</td>
</tr>
<tr>
<td>Ni(FDH)₂Cl₂</td>
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<td>34.10</td>
<td>2.84</td>
<td>20.15</td>
<td>16.68</td>
</tr>
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<td></td>
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<td>33.98</td>
<td>2.79</td>
<td>20.10</td>
<td>16.62</td>
</tr>
<tr>
<td>Cu(FDH)₂Cl₂</td>
<td>7.85</td>
<td>33.64</td>
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</tr>
</tbody>
</table>

* The top line of each analysis is the calculated values, and the bottom line of each analysis is the observed percentage.
### TABLE II  
**PROPERTIES OF THE COMPOUNDS**

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<tr>
<th>Complex</th>
<th>Color</th>
<th>M.P. a</th>
<th>Molecular Wt.</th>
</tr>
</thead>
<tbody>
<tr>
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<td>94 decomp.</td>
<td>491 (Theoretical)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>*484 (Found)</td>
</tr>
<tr>
<td>Mn(FDH)$_2$Cl$_2$</td>
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<td>202 decomp.</td>
<td>348 (Found)</td>
</tr>
<tr>
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<td>light brown</td>
<td>134</td>
<td>349 (Found)</td>
</tr>
<tr>
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<td>brown black</td>
<td>130-132</td>
<td>498 (Found)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>*495 (Found)</td>
</tr>
<tr>
<td>Co(FDH)$_2$Cl$_2$</td>
<td>tan</td>
<td>198-202 decomp.</td>
<td>352 (Found)</td>
</tr>
<tr>
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<td>225 decomp.</td>
<td>352 (Found)</td>
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<td></td>
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</tr>
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</tr>
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<td></td>
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<td>358 (Found)</td>
</tr>
<tr>
<td></td>
<td></td>
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<td>*339 (Found)</td>
</tr>
</tbody>
</table>

a Uncorrected.

* Molecular Weight Found.
B. Infrared Spectra.

Jaffé has shown that one difference between the stability of intermolecular and intramolecular hydrogen bonds is the difference in the magnitude of the entropy change for the bond formation. Jaffé estimated that the entropy change for intermolecular H-bonding is of the order of \(-50\) e.u. per mole in the vapor state (35). Supposedly, most of this entropy change is due to the loss of translational and rotational motions. The entropy change in the liquid or in solution is much smaller because of the loss of translational and rotational freedoms due to the cage effect on the solute molecules. Nevertheless, the entropy change for the intermolecular hydrogen bond is still much larger than the change for the intramolecular bond formation. Consequently, if one considers the entropy change, the formation of intramolecular hydrogen bonding is favored even if such bonds are weaker than the intramolecular hydrogen bonds.

The phenomenon of hydrogen bonding has been investigated extensively through the use of infrared spectroscopy. Consequently, much is known about the types of groups most likely to participate in such bonding, the energies and lengths of the bonds, and the approximate form of the associated potential energy function (36-38). Evidence which substantiates the phenomenon of intramolecular hydrogen bonding between proton donors and unsaturated linkages, including cyclopropane rings and aromatic rings, has been reported by many investigators (39-47).

The energies of intermolecular hydrogen bonds have been
shown to be about three to ten Kcal/mole. Although in some cases the energies, as measured by $\Delta_{\text{X-H}}$, have been estimated to be much less than this lower limit (48).

It should be remembered that as the energy of the hydrogen bond decreases, the importance of other effects such as dipole-dipole association in solutions of high dielectric strength may be as significant as the effects due to hydrogen bonding.

At first glance, there appear to be two possible proton acceptors in 1,3-furfuraldoxime that is shown in structure (VIII). One possibility is the non-bonding electron pair on the oxygen atom of the ring, and the other is the conjugated $\pi$-electron system of the ring. One of the non-bonding pair of electrons is in a $\pi$-molecular orbital involving the furan ring and thus gives the six $\pi$-electrons that are demanded by the concept of aromaticity. However, it is probable that electron density is more localized around the oxygen atom in the ring because of its greater electronegativity. The conclusion is that the hydrogen bond is formed to the $\pi$-electron system at or near the oxygen atom. An examination of molecular models (Fig. 6 and 7) indicates that the position of the hydrogen atom of the oxime in the bidentate bis complexes is not as favorable for extensive hydrogen bonding with the ring as is the position of the hydrogen atom in the monodentate tris complexes. As shown by Figures 1 and 5a,b, the band due to the O-H stretch in the 3200 to 3400 cm$^{-1}$ region of the bidentate bis complexes of the divalent metals is displaced by more than 100 cm$^{-1}$ compared to $\nu$(O-H)
band in the free ligand; the band is still very sharp and intense, and there is only relatively low intensity moderate broadening. In contrast, the band in the 3200-3500 cm\(^{-1}\) region for the monodentate tris complexes is very broad, and the free \(\nu(\text{O=H})\) is completely masked. The absorption band system for the free ligand (Fig. 3) in the region 3200-3500 cm\(^{-1}\) is essentially similar to that for the monodentate tris complex with the significant difference that the band due to the free \(\nu(\text{O=H})\) is observed at \(\sim 3590\) cm\(^{-1}\). Furthermore, the hydrogen bonding in the free ligand is largely intermolecular as is evidenced by the high intensity of band due to hydrogen bonding, and rapid and nonlinear loss of absorbance on dilution was observed. The loss of absorbance on dilution did not follow Beer's law.

The infrared absorption bands of \(\beta\)-furfuraldoxime in mull, \(\beta\)-furfuraldoxime in CCl\(_4\), and the complexes are reported in Table III. The corresponding absorption bands of the structurally related ligand as well as those of furfural, furiloxime, and furan are included for comparative purposes.

It is appropriate to discuss the bands in the infrared region with respect to the predominant functional groups present. These bands considered in order of decreasing energy are as follows: the hydroxyl group (3400-3100 cm\(^{-1}\)), the O\(=\)N (1650 cm\(^{-1}\)), the furan ring, and the N-O (970 cm\(^{-1}\)).

The frequency range generally assigned to the absorption by the free hydroxyl is 3700-3500 cm\(^{-1}\). In oximes, the O-H stretching
frequencies are shifted to lower values, appear in the range 3200-3100 cm\(^{-1}\), and indicates that hydrogen bonding is present (49, 50). The shift in wave numbers from the non-bonded to the hydrogen-bonded hydroxyl peak is a measure of its enthalpy (51). The shift is therefore a quantitative measure of the acidity or basicity of molecules as hydrogen bond donors or acceptors. Huggins and Pimentel (52) have shown that the intensity of the hydrogen-bonded bands is ordinarily proportional to basicity.

The salient feature of the infrared spectra of the free ligand and the transitional metal complexes is the position and band width of the \(\nu(\text{O-H})\). The mull spectrum of the ligand exhibits a very intense broad band from the H-bonding centered at 3175 cm\(^{-1}\) that overlaps the band due to the ring C-H stretch at 3030 cm\(^{-1}\). In contrast to the mull spectrum (Fig. 3a), the CHCl\(_3\) solution spectra (Fig. 3b, 3c) show complete resolution of the free \(\nu(\text{O-H})\), the band caused by H-bonding, and the \(\nu(\text{C-H})\). Furthermore, in Figures 3b and 3c the ratio of the areas under the band due to the free \(\nu(\text{O-H})\), and the band due to the H-bonding was not constant with varying concentration in CHCl\(_3\) which indicate that the H-bonding in the free ligand is primarily intermolecular. This information is in agreement with the n.m.r. results of an investigation published in a recent paper by Wasylichen and Schaefer (53). They cited proton chemical shift and long range coupling data to support the conclusion that the anti isomer of 2-furfuraldoxime exists almost exclusively in the s-cis form in solution, independently of the type of intermolecular
association that occurs. Intramolecular H-bonding apparently is absent in this isomer according to these investigators. Similarly, the syn isomer exists in s-cis and s-trans forms but in roughly equal mixtures in solvents of widely different polarities. These conformational preferences in solution are represented below.

\[
\begin{align*}
\text{(s-cis)} & \quad \leftrightarrow \quad \text{(s-trans)} \\
\text{syn, m.p. 75°} & \\
\text{(s-cis)} & \quad \leftrightarrow \quad \text{(s-trans)} \\
\text{anti, m.p. 91°}
\end{align*}
\]

The following kinds of evidence support the assigned conformational preferences. An oximino-proton n.m.r. signal that appears as a sharp peak at low field, 10.71 p.p.m. independent of concentration, is typical of an intramolecular H-bonded oximino
proton. The oximino-proton signal, if moved to higher field with decreasing concentration, appears as a broad signal at 7.6 p.p.m. and is typical of the dissociation of intermolecularly H-bonded oximes (54).

It is known that benzene solvent molecules tend to avoid electron rich regions of solute molecules (55, 56). In oximes, these regions are in the vicinity of the hydroxyl oxygen, and the proton of the ring situated near the hydroxyl group is expected to display the smallest aromatic solvent induced shift (ASIS).

Wasylischen reports that the ASIS value of H₃ in the anti form of the above conformer is actually negative and has a value of -4.1. This evidence supports the assignment of the s-cis form of the anti isomer as the stable one in solution. The solvent shift is given in Hz and is determined by subtracting the shift in CDCl₃ to low field of internal TMS from the shift in C₆D₆ to low field of internal TMS. In both forms of the syn isomer the H₃ proton is not as close to the hydroxyl group as it is in the s-cis form of the anti isomer. Therefore, the ASIS value (45.8) is much larger and not much different than the determined ASIS values of the other ring protons.

Wasylischen further reports a μ value of 0.67 Debye for the dipole moment by INDO calculations for the planar s-cis form of the anti oxime and μ is 0.61 D if the CHNOH group is twisted to lie 19° above the plane of the furan ring. The 19° angle of twist has been observed in the solid state in the case of anti-p-chlorobenzaldoxime (57, 58). The observed dipole moment of the monomeric
form of the anti isomer is 1.9 D in benzene (59). The calculated dipole moment of the oximes is extremely sensitive to the conformation of the O-H group. Wasylischen notes that if the OH bond in the s-cis form of the anti isomer is twisted 30° out of the plane of the CHNO group and pointed towards the ring, the calculated dipole moment is 3.73 D. He uses this argument to discount the fact that the calculated moment 1.22 D of the s-trans form of the anti oxime cannot be taken to be evidence for the relative stability of this form. If the s-trans form of the anti isomer has the O-H bond turned through 180° to simulate an intramolecular H-bond to the ring oxygen, the INDO dipole moment becomes 4.76 D. Since this value is much larger than the observed value of 1.9 D, the possibility of such H-bonding seems unlikely to occur. Therefore, Wasylischen concludes that intramolecular H-bonding is absent in the s-cis form of the anti isomer and concludes on the basis of INDO calculations that the s-cis form of the anti isomer is 1.7 Kcal/mole more stable than the s-trans anti isomer.

If the ligand, β-FDH, exists chiefly as the s-cis form of the anti isomer in equilibrium with the s-trans form and if complexation occurs preferentially via the two oxygen atoms in the ligand (as shown by our research), then the s-trans form of the anti isomer must be the reactive form of the ligand during complexation. Only in the s-trans form of the anti isomer are the two donor oxygen atoms geometrically favorable for complexation. Obviously, since complexation occurs with the s-trans form of the ligand, some s-cis form is
converted to s-trans form as the concentration of the s-trans is decreased by complexation. Since $K_{eq}$ is a constant, the direction of shift is from s-cis to s-trans as complexation occurs with the s-trans form of the isomer.

In general, the spectra of the complexes are similar except that the spectrum of one complex may be slightly shifted with respect to another. Sen and Dotson (60) have shown that the spectra of complexes that have ligands containing the OH functional group may have three bands corresponding to the free $\nu$(O-H), H-bonding, and the coupling of the OH frequency with one of the symmetry allowed vibrations of the framework of the complex. Furthermore, the band of the free $\nu$(O-H) may or may not be observed because its occurrence depends on the intensity of the other two bands.

In 1952, Rundel and Parasol (61) observed that the O-H stretching frequency bands of glyoximes usually found near 3100 cm$^{-1}$ are shifted to considerably lower frequencies in the case of Ni(II) complexes. This shift was attributed to strong intramolecular hydrogen bonding, and Rundel and Parasol observed that as the OH...O distance decreases, the OH stretching frequency becomes lower in a series of compounds in which the OH...O distance varies progressively. This correlation of frequency versus distance was elaborated later by Nakamoto, Margoshes and Rundel (62, 63). This effect was recently observed in this laboratory Sen and Malone in the Ni(II)PPK complexes.

The free O-H stretching frequency in the free ligand is observed around 3590 cm$^{-1}$ (cf. Table III and Fig. 3), whereas the O-H
stretching frequency in the bidentate bis complexes is observed between 3515 cm\(^{-1}\) and 3250 cm\(^{-1}\). Except for the zinc complex, the band due to the free O-H frequency is superimposed on the associated band (Fig. 1). However, the trend of the shift is generally reversed for the hydrogen bonded band. The associated band is observed at a slightly lower wavenumber in the free ligand than in the complexes and is, of course, much more intense in the free ligand than in the complexes. The foregoing trends of infrared frequency shifts may be interpreted as follows. The shift of \(v(O-H)\) towards a lower wavenumber in the complexes is due to coordination through the oxygen atom and to a small extent is due to hydrogen bonding. The larger shift of the associated band in the free ligand is due to more extensive intermolecular hydrogen bonding in the free ligand.

Krause, et. al., (64) have noted that the broad OH band of a conventional oxime is replaced by multiple bands in the range 3194-2791 cm\(^{-1}\) in the case of syn-phenyl-2-pyridinaldoxime which has the strongest band at 2791 cm\(^{-1}\). The interpretation of this effect was that much stronger hydrogen bonding was involved in this compound than in other oxime systems. Krause also observed a similar behavior in the case of the syn-phenyl-2-pyridylketoxime in that multiple bands due to H-bonding effects are observed over the range 3226-2817 cm\(^{-1}\). Sen and Malone (31) have demonstrated that the essential nature of H-bonding in syn-phenyl-2-pyridylketoxime and its complexes remains the same; H-bonding is intramolecular and is via O-H proton and the phenyl \(\pi\)-electronic system.
β-furfuraldoxime also exhibits a broad band centered at 2820 cm\(^{-1}\) which appears to be resolved in the spectra of the transitional metal complexes into two weak shoulders on the broad band due to the OH stretch. These multiplets appear as shoulders near 3060 cm\(^{-1}\) and 2850 cm\(^{-1}\). However, it is possible that the shoulder near 2850 cm\(^{-1}\) could be an overtone of the O=C band. In addition to the multiplet bands, the ring C-H stretch appears as a shoulder near 3150 cm\(^{-1}\) which is well defined in the spectra of the complexes, but it is overlapped by the broad OH stretch that is shown in the mull spectra of the free ligand. There is also a sharp intense band which appears near 755 cm\(^{-1}\) and is probably caused by the three adjacent ring hydrogen atoms.

X-ray diffraction work (65-67) indicates that syn aldoximes form dimers whereas anti isomers associate to long chains. Usually the latter type of association tends to form stronger hydrogen bonds; the greater bond strength explains the lower frequencies of the anti isomers of aldoximes. In the liquid state all the isomers of the oximes form predominantly cyclic dimers or trimers (68). This association of simple oximes (pK\(_a\) 10.0-12.5) to give dimers in the form of six-membered rings or trimers in the form of nine-membered rings is illustrated by the structures

(Dimer) and (Trimer)
The structure of the long chains that result from the association of the anti isomer may be represented by

\[
\begin{align*}
\text{The magnitude and the trend of the shift of the band due to hydrogen bonding in the mull and the solution spectra of the free ligand is significant. The associated band is shifted by nearly 100 cm}^{-1} \text{ (lower) in the mull spectrum with respect to the band of the solution spectrum indicating more extensive hydrogen bonding in the chain form in the solid phase. Hydrogen bonding in solution, perhaps, lead only to the formation of dimers and trimers.}
\end{align*}
\]

There are two bands that appear near 1650 cm\(^{-1}\) and 950 cm\(^{-1}\) which are assigned respectively to the C=N stretch and the N-O stretch in both the free ligand and the complexes. The band intensity is proportional to the polarity of the group, and the position of the C=N band stretch may be slightly influenced by ring strain. The shift in the C=N stretch of the complexes as compared to that of the free ligand is small and is found to be at the most 30 cm\(^{-1}\) and mostly of the order of 5 to 15 cm\(^{-1}\).

In organic nitroso compounds the N=O stretching band has been found to vary in frequency within rather large limits, 1450 cm\(^{-1}\)
to 1600 cm\(^{-1}\); the position of the band depends to some extent upon the double-bond character of the linkage (49). For simple oximes, the N-O stretching band appears between 930 and 960 cm\(^{-1}\) (69). In some cases of monoximes the N-O stretching band is shifted to 1075-975 cm\(^{-1}\) because of contribution of =\(\overline{\text{C}}\text{-N}=\overline{\text{O}}\cdots\text{H}...\) (70). The N-O stretching band of \(\beta\)-furfuraldoxime appears at 970 cm\(^{-1}\) in the mull spectrum and at 960 cm\(^{-1}\) in the solution spectrum of the free ligand. It is interesting to note that the N-O stretching band near 940 cm\(^{-1}\) appears somewhat lower in the complexes. As the oxime proton becomes more ionic due to H-bonding, there is probably more contribution of \(=\text{N}=\overline{\text{O}}\) to the structure.

The C=N vibration remains essentially unchanged as expected due to its remoteness from the coordination site. If anything, there is possibly a very small shift (\(\sim 5\) cm\(^{-1}\)) of the C=N band towards the higher energy end of the spectrum. This might be due to a limited degree of back bonding resulting from the metal d-electronic contribution to the C=N pi molecular orbital.

The lower energy portions of the spectrum (2000-600 cm\(^{-1}\)) of each complex are very similar; there are only minor variations in each; therefore only the Cu(FDH)\(_2\)Cl\(_2\) spectrum is presented in Figure 4 as a representative spectrum. The lower energy portion of the ligand spectrum is presented in Figure 2 for comparison purposes.

The frequency range 1600-1000 cm\(^{-1}\) for \(\beta\)-furfuraldoxime and its complexes embraces a series of bands due to C=C vibrations. These skeletal in plane C=C vibrations normally appear at approximately
1600, 1580 (shoulder), 1500, 1450 and 1030 cm\(^{-1}\) and appear in the spectra of the free ligand and the complexes. It should be noted that the C=N band is often difficult to identify because there are large variations in intensity of the band and it appears close to the C=C stretching region; oximes usually give C=N stretching bands that are very weak (71).

A band near 1300 cm\(^{-1}\) in the spectra of oximes has been assigned by Palm and Werbin to the OH in-plane deformation mode (50, 69). In fact, the spectra of syn aldoximes in the condensed state or moderately diluted solution contain a medium-strong and broad band between 1290 and 1330 cm\(^{-1}\) which disappears after deuteration or on dilution. A corresponding band is found in the spectra of the anti isomers at slightly higher frequencies. However, between 1420 and 1510 cm\(^{-1}\) another band appears and has a similar characteristic behavior. Spectra of associated O-deuterated oximes show two new bands. One band occurs between 1040 and 1120 cm\(^{-1}\), and in the case of the anti isomer the band appears at higher frequencies. This band is assigned to the OD in-plane deformation. The other band appears between 1318 and 1360 cm\(^{-1}\), but the spectra of C-deuterated aldoximes do not contain it. Consequently, Hadzi and Premru (68) assign this band to the C-H in-plane deformation. The spectra of the corresponding aldehydes also show this band at similar frequencies. Hadzi has shown that the hydroxyl deformation bands in the anti form of furfuraldoxime appear at 1342 and 1294 cm\(^{-1}\) and that the corresponding O-deuterated bands occur at 1342 and 1010 cm\(^{-1}\).
Two bands at 1345 and 1295 cm\(^{-1}\) occur in the spectra of the free ligand in both CHCl\(_3\) and CCl\(_4\) and are assigned to hydroxyl deformation. However, these bands are shifted to 1320 and 1235 cm\(^{-1}\) respectively in the hexachlorobutadiene mull spectrum. This band shift could be explained to be the result of differences due to the type and extent of H-bonding. The free ligand in solution tends to dimerize or trimerize, and in the solid state or mull state the liquid preferentially forms H-bonds in straight chains. These hydroxyl deformation bands in the mull spectra of the complexes differ only slightly, and they are tabulated in Table III.

The C-H in-plane deformation band of both the free ligand and the complexes is consistently sharp and appears near 1380 cm\(^{-1}\).

The existence of two association and deuteration sensitive bands in the spectra of aldoximes has been explained to be due to a strong interaction between the OH and CH (aldehyde) in-plane deformation vibrations. Evidence for the role of the CH deformation is the fact that the ketoximes have only one association and deuteration sensitive band in this region.

The argument advanced for the assignment of the C=N and N-O stretching frequencies is supported by the comparison of the infrared spectra of furan, furil monoxime, furfuraldehyde, and the ligand, \(\beta\)-furfuraldoxime. Obviously, these two bands would be absent in the spectra of furan and furfuraldehyde but would appear in the spectra of furil monoxime and the ligand.
The infrared spectral information is given in Table III and is summarized below.

1) The hydrogen bonding in the bis complexes is not as extensive and strong as the H-bonding in the tris complexes. The OH stretching bands of the bis complexes are narrow, are centered near 3350 cm\(^{-1}\), and are superimposed on the band due to hydrogen bonding. The OH band cannot be observed in the spectrum of the tris complexes as it is completely masked by the broad band due to hydrogen bonding.

2) The zinc complex, Zn(FDH)\(_2\)Cl\(_2\), is the only one of the complexes for which the free OH stretching frequency and the hydrogen bonded band are completely resolved.

3) The C=N stretching frequency at approximately 1650 cm\(^{-1}\) appears at slightly higher frequencies in the spectra of the bis complexes than it does in the spectra of the free ligand and the tris complexes.

4) The N-O stretching frequency near 950 cm\(^{-1}\) was slightly lower in the spectra of the complexes than in the spectra of the free ligand.

5) The band centered near 1385 cm\(^{-1}\) is due to the C-H in-plane deformation mode in both the free ligand and the complexes.

6) The two bands near 1325 and 1250 cm\(^{-1}\) are assigned to the hydroxyl deformation in both the free ligand and the complexes.

7) A sharp intense band near 755 cm\(^{-1}\) is tentatively assigned to the three adjacent hydrogen ring effect.
TABLE III

I.R. SPECTRA IN cm$^{-1}$

<table>
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<tr>
<th>Compound</th>
<th>(OH)$_{\text{free}}$</th>
<th>(OH)$_{\text{assoc.}}$</th>
<th>(C-N)</th>
<th>(C-H)</th>
<th>(OH)</th>
<th>(OH)</th>
<th>(N-O)</th>
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<td>970 s</td>
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<td>3270 s, br</td>
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<td>1375 w</td>
<td>1345 m</td>
<td>1295 w</td>
<td>955 s</td>
</tr>
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<td>1650 w</td>
<td>1380 m</td>
<td>1350 m</td>
<td>1295 w</td>
<td>965 s</td>
</tr>
<tr>
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<td>----</td>
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<td>1320 s</td>
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<td>940 s</td>
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<td>3340 s</td>
<td>1650 s</td>
<td>1380 s</td>
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<td>945 s</td>
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<tr>
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<td>1650 w</td>
<td>1385 m</td>
<td>1320 m</td>
<td>1250 m</td>
<td>940 s</td>
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<tr>
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<td>1645 sh</td>
<td>1390 m</td>
<td>1330 w</td>
<td>1250 br</td>
<td>940 s</td>
</tr>
<tr>
<td>Cr(FDH)$_3$Cl$_3$</td>
<td>----</td>
<td>3200 s, br</td>
<td>1645 sh</td>
<td>1380 m</td>
<td>1320 sh</td>
<td>1240 m</td>
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</tr>
<tr>
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<td>Furan</td>
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<td>Furfural</td>
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<td>----</td>
<td>1350 m</td>
<td>----</td>
<td>----</td>
<td>----</td>
</tr>
<tr>
<td>Furil oxime</td>
<td>----</td>
<td>3360</td>
<td>1650 m</td>
<td>1380 s</td>
<td>1320 m</td>
<td>1250 m</td>
<td>935 s</td>
</tr>
</tbody>
</table>

(a) C$_4$Cl$_6$ mull (b) CHCl$_3$ solution (c) CCl$_4$ solution

(br broad, sh shoulder, w weak, m medium, s strong)
Fig. 1. - Infrared hydroxyl stretching bands for hydrogen bound groups in (a) Mn(FDH)$_2$Cl$_2$
(b) Zn(FDH)$_2$Cl$_2$ (c) Ni(FDH)$_2$Cl$_2$
(d) Pd(FDH)$_2$Cl$_2$ (e) Cu(FDH)$_2$Cl$_2$
(f) Fe(FDH)$_2$Cl$_2$ (g) Co(FDH)$_2$Cl$_2$
Fig. 2. - Infrared low energy bands (2000-600 cm\(^{-1}\)).

(a) \(\beta\)-FDH mull in \(C_4\)Cl\(_6\).

(b) 0.2 M \(\beta\)-FDH in \(CCl_4\).
Fig. 3. - Infrared high energy bands (4000-2000 cm\(^{-1}\)).

(a) $\beta$-FDH mull in C\(_4\)Cl\(_8\).
(b) 0.2 M $\beta$-FDH in CHCl\(_3\).
(c) 0.1 M $\beta$-FDH in CHCl\(_3\).
(d) 0.2 M $\beta$-FDH in CCl\(_4\).
Fig. 4. - Infrared low energy bands of Cu(FDH)$_2$Cl$_2$. 
ABSORBANCE

WAVENUMBER x 10^3 (cm⁻¹)
Fig. 5. - Infrared hydroxyl stretching bands for hydrogen bound groups in the tris complexes.
(a) Cr(FDH)₃Cl₃.  (b) Fe(FDH)₃Cl₃.
(c) Infrared high energy bands for Pd(FD)₂.
Fig. 6. - Framework Model of the tris β-FDH complexes.
Fig. 7. - Framework Model of the bis β-FDH complexes.
C. Conductivity.

The results of conductivity measurements are presented in Table IV, and they lead to the conclusion that these compounds are present in solution predominantly as non-electrolytes. It is interesting to note that the monodentate complexes of chromium and iron in the trivalent state exhibit the highest conductances. The high molar conductances of these complexes are attributable to greater extent of displacement of chloride by solvent molecules. The conductivity data indicates that in these compounds the chlorides are coordinated directly to the metal ion and are displaced by the solvent because the conductivity values for the complexes are all lower than the value for a uni-univalent species of NaI in ethanol.
TABLE IV

MOLAR CONDUCTANCE OF THE M (II) & M (III) COMPLEXES IN ETHANOL

<table>
<thead>
<tr>
<th>Complex</th>
<th>Molar Conductance, cm²/ohm mole*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr(FDH)₃Cl₃</td>
<td>28.2</td>
</tr>
<tr>
<td>Mn(FDH)₂Cl₂</td>
<td>19.0</td>
</tr>
<tr>
<td>Fe(FDH)₂Cl₂</td>
<td>16.1</td>
</tr>
<tr>
<td>Fe(FDH)₃Cl₃</td>
<td>26.9</td>
</tr>
<tr>
<td>Co(FDH)₂Cl₂</td>
<td>16.3</td>
</tr>
<tr>
<td>Ni(FDH)₂Cl₂</td>
<td>21.2</td>
</tr>
<tr>
<td>Cu(FDH)₂Cl₂</td>
<td>10.2</td>
</tr>
<tr>
<td>Zn(FDH)₂Cl₂</td>
<td>1.1</td>
</tr>
</tbody>
</table>

* For ca. 10⁻³ molar solutions at 20°C. Reference value for NaI in absolute ethanol is 35 cm²/ohm-mole.
TABLE V
THEORETICAL AND OBSERVED MAGNETIC MOMENTS FOR THE M(II) AND M(III) COMPLEXES IN THE SOLID STATE

<table>
<thead>
<tr>
<th>Complex</th>
<th>Config</th>
<th>Ground State</th>
<th>Free Ion Term</th>
<th>$\mu_s$</th>
<th>$\mu_s + 1$</th>
<th>Obsd. $\mu_{\text{eff}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr(FDH)$_3$Cl$_3$</td>
<td>d$^3$</td>
<td>$^4F$</td>
<td></td>
<td>3.87</td>
<td>5.20</td>
<td>3.94</td>
</tr>
<tr>
<td>Mn(FDH)$_2$Cl$_2$</td>
<td>d$^5$</td>
<td>$^6S$</td>
<td></td>
<td>5.92</td>
<td>5.92</td>
<td>5.96</td>
</tr>
<tr>
<td>Fe(FDH)$_2$Cl$_2$</td>
<td>d$^6$</td>
<td>$^5D$</td>
<td></td>
<td>4.90</td>
<td>5.48</td>
<td>5.41</td>
</tr>
<tr>
<td>Fe(FDH)$_3$Cl$_3$</td>
<td>d$^5$</td>
<td>$^6S$</td>
<td></td>
<td>5.92</td>
<td>5.92</td>
<td>5.71</td>
</tr>
<tr>
<td>Co(FDH)$_2$Cl$_2$</td>
<td>d$^7$</td>
<td>$^4F$</td>
<td></td>
<td>3.88</td>
<td>5.20</td>
<td>5.03</td>
</tr>
<tr>
<td>Ni(FDH)$_2$Cl$_2$</td>
<td>d$^8$</td>
<td>$^3F$</td>
<td></td>
<td>2.83</td>
<td>4.47</td>
<td>3.44</td>
</tr>
<tr>
<td>Cu(FDH)$_2$Cl$_2$</td>
<td>d$^9$</td>
<td>$^2D$</td>
<td></td>
<td>1.73</td>
<td>3.00</td>
<td>1.79</td>
</tr>
<tr>
<td>Zn(FDH)$_2$Cl$_2$</td>
<td>d$^{10}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>diam.</td>
</tr>
</tbody>
</table>

* Magnetic moment values in B.M. units. Reference Hg[Co(CNS)$_4$]
$\chi_{20°} = 16.44 \times 10^{-6}$ c.g.s. (75).
D. Magnetic Susceptibilities.

It has been shown that ligands containing simple sigma bonding donor atoms such as nitrogen and oxygen usually form high spin complexes (72, 73). The magnetic moments shown in Table V indicate that all the compounds are high spin compounds (74, 75). The magnetic moments of iron (III), cobalt (II), and nickel (II) complexes exceed the spin-only value, the the difference is the result of the orbital angular momentum contribution. The remaining complexes have magnetic moments which have the same order of magnitude as that of the spin-only moment values.

E. Bonding.

The ligand, β-FDH, offers three donor atoms that could be possible sites for bonding to the metal atom. These sites are the oxygen atom of the furan ring, the acyclic oxygen atom and the nitrogen atom. If the assumption is made that one donor atom is the oxygen in the furan ring, steric conditions alone preclude bonding via the nitrogen atom in the bidentate case of the anti form of the ligand. A framework model construction suggests that the acyclic oxygen donor atom is in a more favorable stereo position than the nitrogen atom for bond formation to form a six-membered ring. This structure is represented by
and the charge on the metal ion is satisfied by the coordinated chloride ions.

Bryson and Dwyer prepared the palladium complex of $\beta$-FDH in an acidic medium, hydrochloric acid solution of sodium chloropalladite, to yield the yellow bisfurfuraldoxime palladous chloride complex. Bryson and Dwyer offered the indefinite structure

$$\begin{align*}
\text{H}_2 & \quad \text{Cl} \quad \text{NO} \cdot \text{C}_6\text{H}_4\text{O} \\
\text{Pd} & \quad \text{NO} \cdot \text{C}_6\text{H}_4\text{O} \\
\text{Cl} & \quad \text{Cl}
\end{align*}$$

which indicates the uncertainty of the position of two hydrogen atoms. This palladium complex, prepared in acid medium according to the procedure prescribed by Bryson and Dwyer, yields an infrared spectrum almost identical to the infrared spectra of the bis complexes of the divalent metals prepared in only ethanolic medium in this investigation. A comparison of Figure 1d with Figures 1a,b,c,e,and f indicates that if complex formation occurs in ethanol medium, the oxime proton is present and is hydrogen bonded.
Moreover, if the bisfurfuraldoxime palladous chloride compound prepared in acid medium is refluxed with sodium acetate in boiling acetone/methanol solution, the two chlorine atoms are eliminated with the formation of a darker yellow, highly insoluble bisfurfuraldoxime palladium complex, \( \text{Pd(C}_5\text{H}_4\text{O}_2\text{N)}_2 \). This structure proposed by Bryson and Dwyer is

![Chemical structure diagram]

Obviously, the loss of the oximino-proton in a basic solution necessitates loss of H-bonding. The infrared spectrum of the compound \( \text{Pd(C}_5\text{H}_4\text{O}_2\text{N)}_2 \) prepared according to the procedure of Dwyer, is shown in Figure 5C. The disappearance of the OH stretching band shows the complete loss of H-bonding in this compound.

Chelate formation through the two oxygen atoms in the ligand is indicated by the comparison of the infrared spectra of the free ligand with that of the complexes. The infrared spectrum of the palladium complex prepared in acid medium and the infrared spectra of the metal complexes prepared in ethanolic solution are very similar.
The C=N vibrational band positions of the complexes and of the free ligand are nearly the same. If bonding through the nitrogen atom to the metal occurs, a significant shift in the v(C=N) caused by an inductive effect should be expected. However, a significant shift of the frequency of the free OH towards a lower wavenumber in the complexes is observed, and this shift in frequency is due to coordination through the oxygen atom and to a small extent is due to hydrogen bonding.

F. Electronic Spectra.

The near-infrared, visible and ultraviolet absorption bands of the complexes in nujol paper mulls, ethanol or DMF solutions were recorded. The solubility of the complexes is small and consequently the quality of the spectra was in general rather poor, and the resolution of the bands of the mull spectra was not good. The electronic spectral features are summarized in Table VI, and some spectral assignments for the complexes are presented in Table VII. The spectral features of the complexes strongly resemble those of the hexaaquo ions, and the band energies of M(H₂O)₆ ions are given for comparison (76).

The resolution of spectra of the Mn (II) and Fe (III) was extremely poor. These isoelectronic ions that have d⁵ configuration in octahedral symmetry have a ⁶A₁g ground term. Since there is no spin-allowed transition in these complexes, the molar extinction coefficients are expected to be small. Charge transfer bands in the near ultraviolet spectra of iron (III) complexes often have strong
low energy wings in the visible region which tend to obscure the very weak, spin-forbidden d-d bands. Since the spectra of these two species were poorly resolved, no attempt can be made to suggest band assignments for the manganese (II) and iron (III) complexes.

The spectra of nickel (II) and cobalt (II) complexes in mull indicate that the complexes are octahedral symmetry, but the spectral features of the nickel (II) and the cobalt (II) complexes in different concentrations of DMF were such that they seemed to resemble features of both octahedral and tetrahedral configurations. This configurational change in going from a solid phase in the mull to a solution phase in DMF is noteworthy, and the extent to which solvents react by ligand displacement with the solute is perhaps underestimated. Buffagni and Dunn have reported that a [CoCl₄]²⁻ salt dissolved in DMF has a weak band near 5300 Å which is usually associated with an octahedral species. This band disappears when chloride is added to the solution; the octahedral complex is transformed into a tetrahedral form. The species that is postulated to be [CoCl₃(DMF)]⁻ exists in equilibrium with the octahedral complex; the equilibrium is indicated by an isosbestic point in the series of absorption spectra.

The asymmetry of the band assigned to the ²Eₕ → ²T₂ₕ transition is probably due to the Jahn-Teller effect of the distorted octahedral Cu (II). A charge transfer band centered at 37,800 cm⁻¹ that tails off into the blue portion of the visible spectrum imparts a red-brown color to the complex.
### TABLE VI

**ABSORPTION-BAND POSITIONS OF ELECTRONIC SPECTRA**

**FOR THE M(II) AND M(III) COMPLEXES**

<table>
<thead>
<tr>
<th>Complexes</th>
<th>Phases</th>
<th>Band Energies, cm⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr(FDH)₃Cl₃</td>
<td>S</td>
<td>15,400; 21,500; 36,400</td>
</tr>
<tr>
<td></td>
<td>L*</td>
<td>15,400; 21,500</td>
</tr>
<tr>
<td>Fe(FDH)₂Cl₂</td>
<td>S</td>
<td>10,420</td>
</tr>
<tr>
<td></td>
<td>L</td>
<td>10,640</td>
</tr>
<tr>
<td>Co(FDH)₂Cl₂</td>
<td>S</td>
<td>8,300; 19,200; 22,200</td>
</tr>
<tr>
<td></td>
<td>L*</td>
<td>8,300; 15,150; 17,250</td>
</tr>
<tr>
<td>Ni(FDH)₂Cl₂</td>
<td>S</td>
<td>8,000; 14,500; 24,300</td>
</tr>
<tr>
<td></td>
<td>L*</td>
<td>8,000; 14,500; 24,300</td>
</tr>
<tr>
<td>Cu(FDH)₂Cl₂</td>
<td>S</td>
<td>11,750</td>
</tr>
<tr>
<td></td>
<td>L</td>
<td>11,750</td>
</tr>
<tr>
<td>Zn(FDH)₂Cl₂</td>
<td>S</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>L</td>
<td>-</td>
</tr>
</tbody>
</table>

L - Refers to the liquid spectra, using ethanol as a solvent.

L* - Refers to the liquid spectra, using DMF as a solvent.

S - Refers to the solid state spectra, i.e., filter paper mulls.
### TABLE VII

**SPECTRAL ASSIGNMENTS FOR METAL COMPLEXES OF $\beta$-FURFURALDOXIME**

<table>
<thead>
<tr>
<th>Cation</th>
<th>Transition</th>
<th>$M(H_2O)\nu\chi_m$</th>
<th>$M(FDH)<em>\chi Cl</em>\chi$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr(III)</td>
<td>$^4A_{2g}(F) \rightarrow ^4T_{2g}(F)$</td>
<td>17,000 cm$^{-1}$</td>
<td>15,400 cm$^{-1}$</td>
</tr>
<tr>
<td></td>
<td>$^4A_{2g}(F) \rightarrow ^4T_{1g}(F)$</td>
<td>24,000</td>
<td>21,500</td>
</tr>
<tr>
<td></td>
<td>$^4A_{2g}(F) \rightarrow ^4T_{1g}(P)$</td>
<td>37,000</td>
<td>36,400</td>
</tr>
<tr>
<td>Fe(II)</td>
<td>$^5T_{2g} \rightarrow ^5E_g$</td>
<td>10,000</td>
<td>10,400 10Dq</td>
</tr>
<tr>
<td>Co(II)</td>
<td>$^4T_{1g}(F) \rightarrow ^4T_{2g}(F)$</td>
<td>8,000</td>
<td>8,300</td>
</tr>
<tr>
<td></td>
<td>$^4T_{1g}(F) \rightarrow ^4A_{2g}(F)$</td>
<td>19,600</td>
<td>19,200</td>
</tr>
<tr>
<td></td>
<td>$^4T_{1g}(F) \rightarrow ^4T_{1g}(P)$</td>
<td>21,600</td>
<td>22,200</td>
</tr>
<tr>
<td>Ni(II)</td>
<td>$^3A_{2g}(F) \rightarrow ^3T_{2g}(F)$</td>
<td>8,700</td>
<td>8,000</td>
</tr>
<tr>
<td></td>
<td>$^3A_{2g}(F) \rightarrow ^3T_{1g}(F)$</td>
<td>14,500</td>
<td>14,500</td>
</tr>
<tr>
<td></td>
<td>$^3A_{2g}(F) \rightarrow ^3T_{1g}(F)$</td>
<td>25,300</td>
<td>24,300</td>
</tr>
<tr>
<td>Cu(II)</td>
<td>$^2E_g \rightarrow ^2T_{2g}$</td>
<td>12,000</td>
<td>11,750 10Dq</td>
</tr>
</tbody>
</table>
CONCLUSIONS

β-furfuraldoxime has been shown to be a useful ligand in the formation of the complexes of the first row transitional metals. Other investigators have shown that, with the exception of the palladium metal, the syn form of the ligand fails to yield any complex compounds. The syn isomer rearranges under the influence of the metal to yield a complex of the anti oxime.

The isomer used in this investigation was verified by the melting point to be the anti form of the ligand. The role of the ligand, whether monodentate or bidentate, seemed to depend on the charge of the metal ion, and the charge of the central metal was satisfied by coordinated chlorine atoms. All the complexes that were prepared were shown to be non-electrolytes by means of conductance experiments, and the electronic spectra indicated that the complexes have octahedral symmetry. In the case of the trivalent metals that have coordination number of six, the ligand seemed to be monodentate in the complex. In the case of the divalent metals, the ligand was bidentate in the complex. Since the oximino proton of the ligand was retained in ethanolic medium, the ligand coordinates as a neutral species.

With the exception of the diamagnetic zinc complex, all the complexes had high spins. The capacity of β-furfuraldoxime to cause d-orbital splitting approximates that of water as a ligand.

The broad OH stretching band shows that the extent of
hydrogen bonding in the tris complexes is indeed much greater than that in the bis complexes; framework models show geometries that are consistent with this interpretation of relative extent of hydrogen bonding. The elemental analyses indicate that the ligand is monodentate in tris complexes and bidentate in the bis complexes. Cryoscopically determined molecular weights indicate that the complexes are monomeric.

The specificity of a ligand and the preferred geometry of a complex are functions of a large number of parameters such as the nature of the functional groups, the stereoisomerism of the ligand, the reaction medium and conditions, and the valence state of the metal. Since numerous factors are involved in complexation, it is only possible to make some generalized statements about the bonding sites in the ligands formed by the oximes. For example, 2-furfuraldoxime complexes almost exclusively as the anti isomer, and the bonding is proposed to occur preferentially through the two oxygen atoms in the ligand. In contrast to this example, it has been shown that phenyl-2-pyridylketoxime reacts as a ligand only in the syn form of the isomers, and bonding occurs through the two nitrogen atoms in the molecule. However, dioximes and monoximes that have a donor atom in the same molecule provide a series of useful bidentate ligands for study. For example, substitution of a sulfur atom for the oxygen atom in furfuraldoxime yields thiophenealdoxime. This ligand which differs by atom substitution should form complexes that will provide information about the function of the ligand, its stereoisomerism, and its structure on the bonding in the complex. In conclusion if may be said that our current knowledge is not comprehensive enough to precisely define the role of each of the foregoing parameters in complexation.
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VITA

Max Earl Pickerill was born on June 26, 1925 in Parsons, Kansas, where he received his elementary and secondary education. After three years service as a radioman in the U. S. Navy during World War II, he graduated from Parsons Junior College in 1948. He attended Kansas State College at Pittsburg, and he obtained the B. S. degree in 1951. He taught chemistry in several high schools, and he obtained the M. S. degree from Fort Hays Kansas State College in 1953. He joined the faculty at Northern Oklahoma Junior College in 1954, and he was employed as a research chemist during the summers by Continental Oil Company in Ponca City, Oklahoma. In 1960 he joined the faculty at The College of Emporia located in Emporia, Kansas.

During the summers from 1965 to 1970, he did graduate study at Louisiana State University as a participant in summer institutes and research participation programs supported by the National Science Foundation. He continued graduate study during the years 1970 and 1971 in full-time residence at Louisiana State University where he is presently a candidate for the Doctor of Philosophy degree.

He and his wife, Maxine, are the proud parents of six children to whom this dissertation is dedicated. At the time of this writing, they presently have three grandchildren.

Mr. Pickerill returned to The College of Emporia as Head of the Department of Chemistry in September, 1972.
EXAMINATION AND THESIS REPORT

Candidate: Max Earl Pickerill

Major Field: Chemistry

Title of Thesis: Transition Metal Complexes of β-Furfuraldoxime

Approved:

Major Professor and Chairman

Dean of the Graduate School

EXAMINING COMMITTEE:

Date of Examination: November 30, 1972