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PALLADIUM COMPLEXES OF SYMMETRICAL
ALKYL KETOXIMES AND ETHERATES

BY

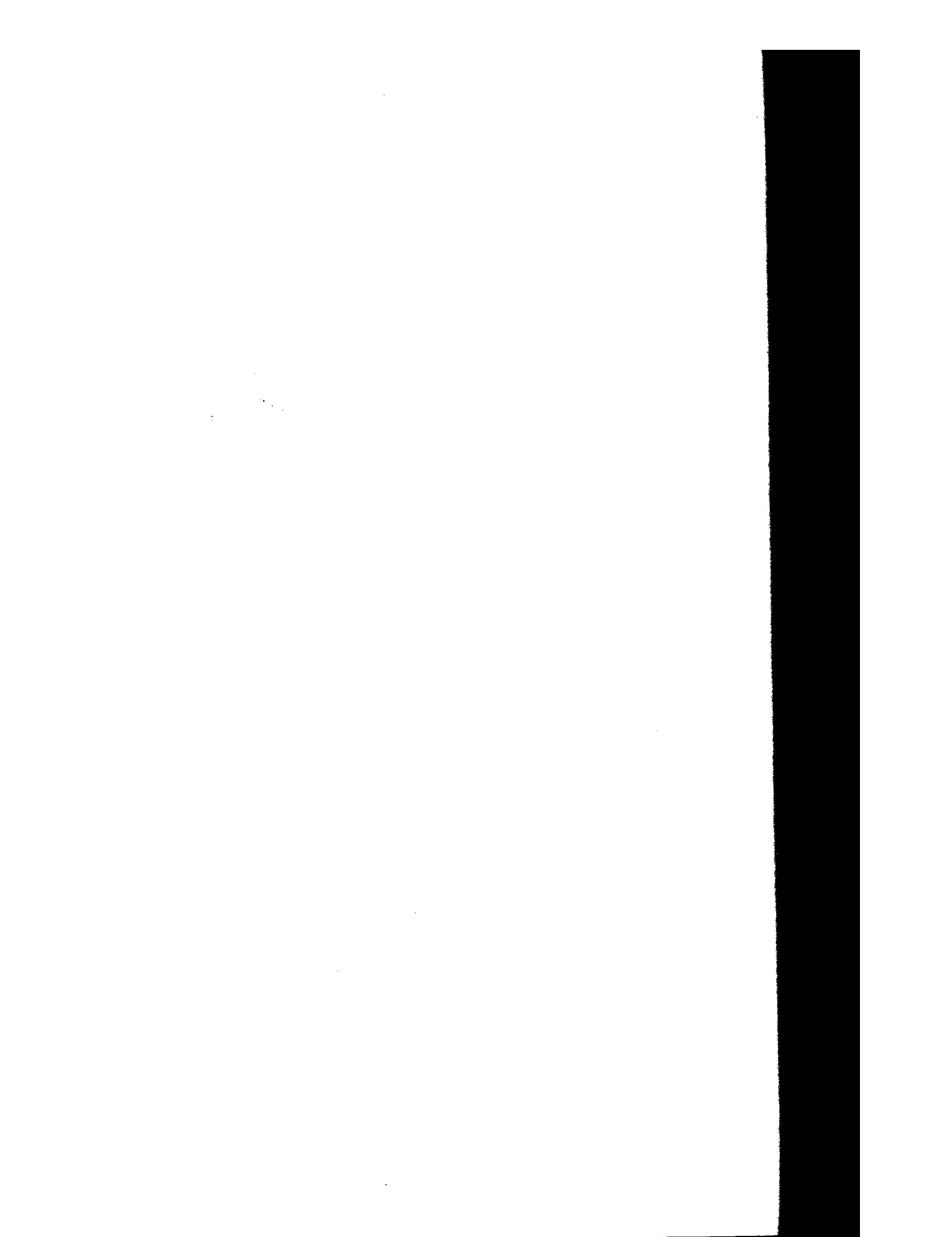
RONALD A. DIMENNA

A Thesis

Submitted to the Faculty of Graduate Studies through
the Department of Chemistry in Partial Fulfillment
of the Requirements for the Degree of Master
of Science at the University of
Windsor

Windsor, Ontario

1971



This thesis has been examined and approved by

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354485

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CHAPTER I

INTRODUCTION

Many coordination compounds of transition metal elements with ligands, having oxygen and/or nitrogen as donors, have been prepared. These works are surveyed in books on coordination chemistry such as those by Bailor, Jorgensen, Jones and others (1, 2, 3).

The coordination ability of the oxime group and the very strong donor properties of the oxime nitrogen are well known (1). Oximes, in general, react selectively with metals at certain pH values. Symmetrical aliphatic oximes and their corresponding etherates react with divalent palladium in acid chloride solution to form stable complexes. The oxime group (C=N-OH) and the etherate group (C=N-OR), where R = CH₃, exhibit a strong coordinating ability for palladium (II).

Palladium (II) usually shows a coordination number of four in its complexes giving squared planar complexes such as Pd(NH₃)₄⁺² and PdI₄⁻². Palladium chloride readily coordinates many ligands such as amines, oximes, phosphines and sulfides to fill two of the sites around the metal.

Thus coordination of two molecules of p-aminoacetophenone (through the amino groups) to palladium in palladium (II) chloride gives the water insoluble complex $(\text{NH}_2\text{C}_6\text{H}_4\text{COCH}_3)_2\text{PdCl}_2$ (4).

The purpose of the work described in this thesis was to determine the reaction between divalent palladium and aliphatic oximes and their etherates as to stoichiometry and nature of the metal to ligand bond.

It is well known that the infrared spectrum of a molecule is characteristic of the entire molecule; however, certain groups of atoms produce bands or peaks with a characteristic absorption frequency regardless of the structure of the rest of the molecule (5).

There are two types of molecular vibrations of interest: stretching and bending. A stretching vibration is a rhythmical movement along the bond axis such that the interatomic distance is increasing or decreasing. A bending vibration may consist of a change in bond angles between the bonds with a common atom, or the movement of a group of atoms with respect to the remainder of the molecule without movement of the atoms in the group with respect to one another (5).

Studies of vibrational spectra provide valuable information about molecular structure and chemical bonding

in coordination compounds (6). A comparison of the infrared spectra of the free and complexed ligands can be used to determine the type of bonding in a series of metal complexes (7). The nature of the metal to ligand bond can be determined by vibrational frequency shifts occurring between the free ligand and its corresponding metal complex.

The principal absorption peaks of prime importance in this study are those of the free oxime functional group (unbonded oxime), $C=N-OH$, the free etherate functional group (unbonded etherate), $C=N-OR$ where $R = CH_3$, and the bonded functional groups of each oxime and etherate (coordination of the free functional group to a palladium (II) ion).

Proposed structures are based on elemental analysis, infrared spectral studies and changes in pH during reaction.

The investigation carried out is restricted to the reaction of bivalent palladium to aliphatic oximes and etherates as to stoichiometry and chemical bonding. The overall objective of this work was the application of these reagents to the analytical problem of selectively separating palladium from other metals (under certain conditions of pH) in macro amounts by solvent extraction.

The reactivity of palladium (II) to aliphatic oximes

and etherates is of prime importance in a study before these reagents can be effectively applied to the analytical problem of selective separation.

CHAPTER II

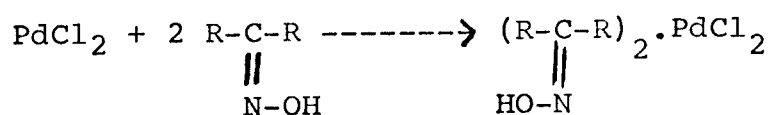
EXPERIMENTAL

The complex formation between divalent palladium and symmetrical aliphatic oximes and their corresponding etherates was studied.

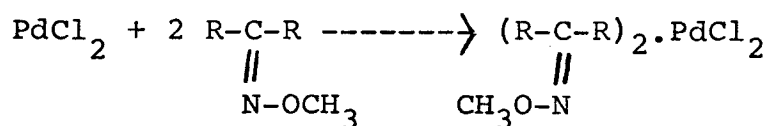
The oximes were prepared by reaction of the ketone with hydroxylamine hydrochloride, using a modification of the method of Shriner and Fuson (8). The etherates were prepared by reacting the ketone with methoxyamine (9). The etherates and oximes obtained were subsequently reacted with palladium (II) chloride under acidic conditions utilizing a modification of the procedure of Lee (10).

At pH 3.0, when solutions containing stoichiometric amounts of oxime or etherate and palladium (II) chloride were mixed, a yellow crystalline complex formed in good yield.

The general stoichiometric equation for oxime palladium complexation is:



The corresponding equation for the etherate palladium complexation is:



In most cases of preparation, yield was sacrificed for purity. Compounds were identified and purity checked by the melting points, boiling points and the presence or absence of C=N, C=O and O-H stretching modes in the infrared region. Gas chromatography was used to determine purity where possible.

REAGENTS AND APPARATUS

Reagents

Acetoxime (highest purity from Eastman Kodak Co.) was used without further purification.

Acetone, A.C.S. grade, diethylketone, di-n-propylketone, di-n-butylketone, reagent grades, were used.

Methoxyamine hydrochloride (Eastman, highest purity) was used.

Anhydrous palladium (II) chloride (Fisher, highest purity) was used.

Hydroxylamine hydrochloride, A.C.S. grade, was purchased from Mallinckrodt chemical works.

Ethanol, 95% and 99%, was used.

Hydrochloric acid and potassium hydroxide, A.C.S. grades, were utilized.

Distilled water was used in all cases.

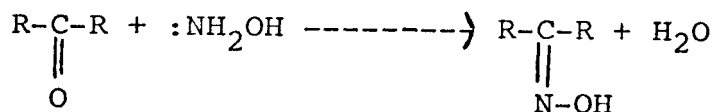
Instruments

All infrared spectra were obtained with a Beckman IR-12 infrared spectrometer. One percent cesium iodide or potassium bromide discs were used. In cases of liquids, neat samples in cesium iodide or polyethylene film cells were used. All samples were also run in spectronic grade chloroform in 5 - 10% w/v concentration. A Sargent model LS pH meter was used for all pH measurements. A Perkin Elmer model 154 gas chromatograph equipped with a 10% polypropylene glycol on Chromosorb W column, six feet in length, was used for purity determinations.

PREPARATION OF OXIMES

Symmetrical aliphatic ketones react with hydroxylamine hydrochloride to give the corresponding oximes.

The basic reaction is:



where R = CH₃, C₂H₅, n-C₃H₇, n-C₄H₉.

Preparation of Diethylketoxime

To a 250-ml round bottom flask, equipped with a reflux condenser, were added 33 g (0.38 mole) of diethylketone dissolved in 50 ml of 95% ethanol, 28 g (0.40 mole) of hydroxylamine hydrochloride dissolved in 40 ml of water and 16 g (0.40 mole) of sodium hydroxide dissolved in 40 ml of water. The mixture was refluxed for 3 hours. At the end of this time the resulting two layers were separated. The oily top layer was dried with anhydrous calcium chloride and distilled to give the oxime (a clear, colourless liquid) in good yield. The oxime was collected at a boiling point range of 158 - 160°, the literature value being 162 - 163° (11). Infrared analysis indicated C=N and O-H stretching modes, but no C=O stretching mode. Gas chromatographic analysis indicated no ketone in the sample.

Preparation of Di-n-propylketoxime

To a 250-ml round bottom flask, equipped with a reflux condenser, were added 16 g (0.14 mole) of di-n-propylketone dissolved in 100 ml of 95% ethanol, 10.5 g (0.15 mole) of hydroxylamine hydrochloride dissolved in 30 ml of water and 6.0 g (0.15 mole) of sodium hydroxide in 30 ml of water. The resulting mixture was refluxed for 3 hours. The excess ethanol was evaporated off until two layers

formed. The oily top layer was separated and dried with anhydrous calcium chloride. The resulting clear, colourless, oily liquid was distilled to obtain the oxime in good yield. The oxime was collected over a boiling range of $187 - 188^{\circ}$, the literature value being 192° (12). Infrared analysis indicated C=N and O-H stretching, but no C=O stretching frequency. Gas chromatographic analysis indicated no ketone impurity in the synthesized oxime.

Preparation of Di-n-butylketoxime

A homogeneous solution of 16.6 g (0.12 mole) of di-n-butylketone dissolved in 100 ml of 95% ethanol, 9.1 g (0.13 mole) hydroxylamine hydrochloride dissolved in 30 ml of water, and 5.2 g (0.13 mole) sodium hydroxide dissolved in 25 ml of water were refluxed for 3 hours in a 250-ml round bottom flask equipped with a reflux condenser. The excess ethanol was allowed to evaporate until two layers formed. The oily top layer was separated and dried with anhydrous calcium chloride. The resulting clear, colourless, oily liquid was vacuum distilled to obtain the oxime in good yield. The oxime was collected over a boiling range of $88 - 90^{\circ}$ at a pressure of 1.0 mm of Hg, the literature value being 124.5° at a pressure of 15 mm of Hg (13). Infrared spectral analysis indicated no ketone in the prepared oxime.

PREPARATION OF ETHERATES

A.C.S. grade acetone and diethylketone were reacted with methoxyamine and the corresponding etherates (O-methyl ethers) were formed. These etherates were prepared according to the procedure of Jones and Major (9).

The basic reaction equation is:



Preparation of Methoxyamine

Methoxyamine is a low-boiling, clear, colourless liquid having a distinct fishy odour. The methoxyamine was liberated from methoxyamine hydrochloride by a concentrated solution of potassium hydroxide.

A modified procedure of Jones and Major (14) was used to prepare the methoxyamine. A solution of 10 g (0.18 mole) potassium hydroxide in 10 ml of water was added to 8.5 g (0.11 mole) O-methylhydroxylamine hydrochloride and the mixture was distilled through hot potassium hydroxide pellets as outlined in Figure 1. The yield was 80% (4.0 g) and the methoxyamine was collected at a boiling point range of 47 - 49^o, the literature value being 49^o (14, 15). If the amounts of the starting materials are doubled, the yield apparently decreases due

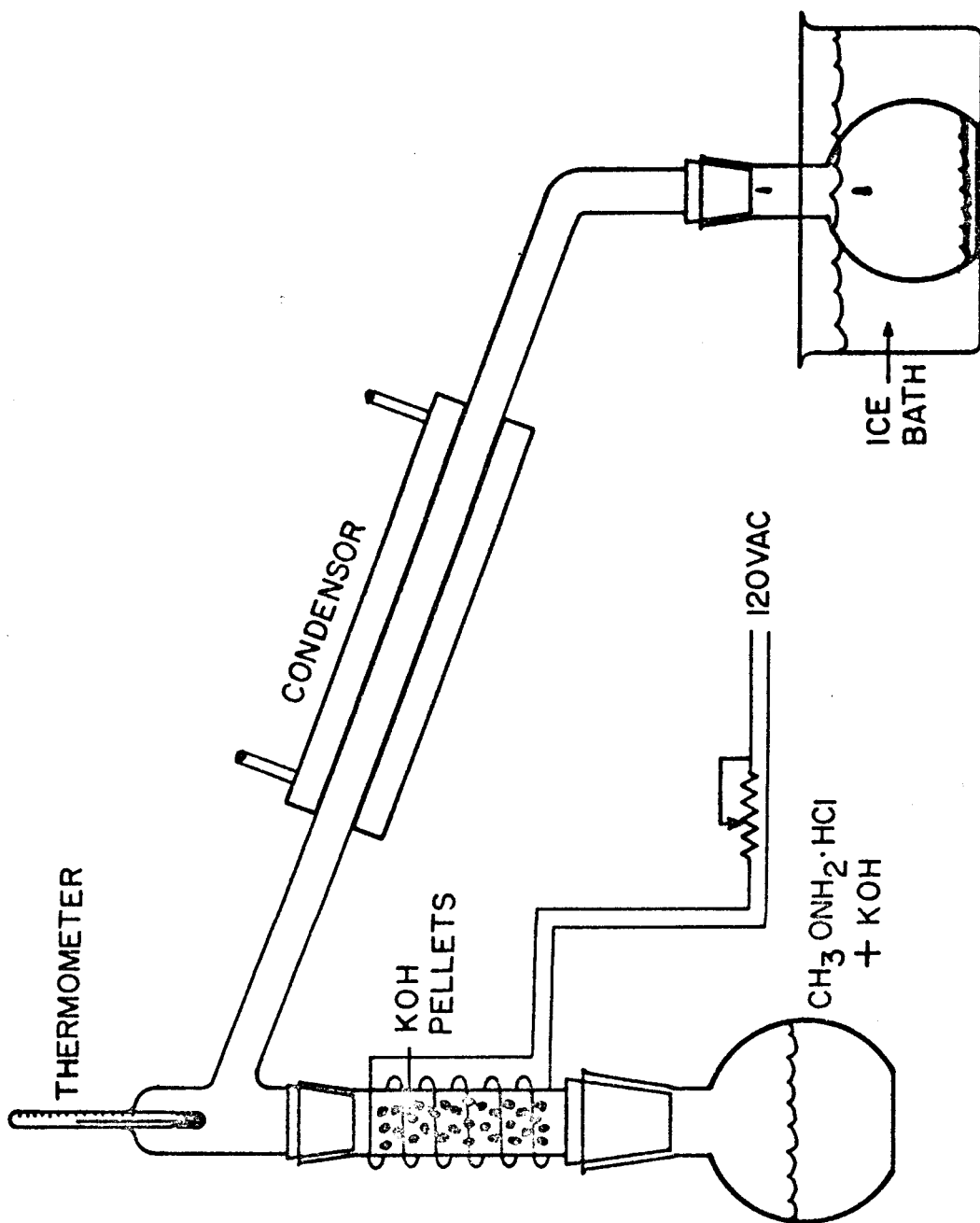


Fig. 1: DISTILLATION APPARATUS

to the increased solubility of the amine in the potassium hydroxide mixture.

Preparation of O-Methylacetoxime

To 6.0 g (0.13 mole) of O-methylhydroxylamine (methoxyamine) was added 7.5 g (0.13 mole) of A.C.S. grade acetone. The mixture was placed in a 50-ml closed reaction flask and allowed to stand for 4 days. When the acetone was added to the methoxyamine, the reaction flask became very hot. During the 4 days, two layers formed. The two layers were then poured over anhydrous calcium chloride and left for 30 minutes so that the bottom layer (presumably water) could be absorbed. The unabsorbed, clear, colourless liquid was decanted and subsequently dried again over anhydrous calcium chloride and then distilled, using a micro-distillation apparatus. The product was collected at $71 - 72^{\circ}$, the literature value being $72 - 74^{\circ}$ (9). The product yield was 70%. Infrared analysis indicated C=N stretching and no O-H or C=O stretching frequency. Gas chromatographic analysis indicated no ketone in the prepared etherate.

Preparation of O-Methyldiethylketoxime

A mixture of 6.0 g (0.13 mole) of methoxyamine added to 11.2 g (0.13 mole) of diethylketone was allowed to

stand for 4 - 5 days in a 50-ml closed reaction flask. During this time, two layers formed. The two layers were poured over anhydrous calcium chloride and allowed to stand for 30 minutes. The resulting unabsorbed, clear, colourless liquid was decanted, dried again over anhydrous calcium chloride and distilled and collected over 116 - 117^o boiling range, the literature value being 116 - 117^o (9). The yield was 66%. The infrared spectral analysis indicated C=N stretching and no O-H or C=O stretching modes. Gas chromatographic analysis indicated one compound, that is, no ketone peak could be observed in the chromatogram.

SYNTHESES OF PALLADIUM COMPLEXES

Aliphatic oximes and etherates through the nitrogen and oxygen donor atoms possess the ability to form coordination complexes with divalent palladium. Stoichiometric amounts of oxime and etherate were reacted with a 10% excess of palladium (II) ion at a pH 3.0. The excess palladium (II) ion was used to determine whether or not the ligands would quantitatively react with palladium (II). All elemental analysis of carbon, hydrogen, nitrogen and chloride was carried out by Midwest Microlab Inc., Indianapolis, Indiana. The percentage of palladium in the complex was determined gravimetrically by the method

of Lee (16).

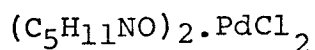
Synthesis of Dichlorobis (acetoxime-N,N') palladium (II) --
(C₃H₇NO)₂.PdCl₂

To 0.44 g anhydrous palladium (II) chloride (10% excess), in a 250-ml beaker, was added 20 ml of 6 N hydrochloric acid. The mixture was thoroughly stirred and then it was very gently heated on a hot plate until a clear, reddish-brown solution was obtained. The volume of the solution was adjusted to 50 ml with water and the pH brought to 3.0 by the titrimetric addition of 6 N potassium hydroxide solution. To 50 ml of water in a 250-ml beaker was added 0.33 g of acetoxime. The pH of this solution was adjusted to 3.0 by the dropwise addition of a 10% hydrochloric acid solution. The palladium (II) chloride solution was then slowly added with continuous stirring to the acetoxime solution. The pH of the mixture during and after addition of the palladium (II) chloride was monitored with a pH meter. A fine yellow precipitate formed within 5 minutes of stirring after the complete addition of the palladium (II) chloride and stirring was continued for another hour. The yellow precipitate was vacuum filtered and washed with three 10-ml portions of a 5% hydrochloric acid solution followed by three 10-ml portions of water solution (pH 3.0). The complex was vacuum dried overnight over anhydrous

calcium sulfate. The yield of the yellow complex was 60% (0.43 g) and it melted at 180 - 190^o with decomposition.

Analysis	Theory - %	Found
C	22.28	21.97
H	4.36	4.37
N	8.66	8.48
Cl	21.92	21.90
Pd	32.90	i) 32.66 ii) 32.20

Synthesis of Dichlorobis (diethylketoxime-N,N') palladium (II) --



To 0.44 g anhydrous palladium (II) chloride (10% excess), in a 250-ml beaker, was added 20 ml of 6 N hydrochloric acid. The mixture was gently heated on a hot plate until a clear, reddish-brown solution was obtained. The volume of the solution was adjusted to 50 ml with water and the pH brought to 3.0 by the titrimetric addition of 6 N potassium hydroxide solution. To 50 ml of a 5% ethanol-water mixture (2.5 ml of 95% ethanol and 47.5 ml water), in a 250-ml beaker, was added 0.45 g diethylketoxime. The pH of this solution was adjusted to 3.0 by the dropwise addition of a 10% hydrochloric acid solution. The palladium (II) chloride solution was slowly added with

continuous stirring to the diethylketoxime solution.

The pH of the mixture, during and after addition of the palladium (II) chloride solution, was monitored with a pH meter. A fine yellow precipitate formed within 5 minutes of the complete addition of the palladium (II) chloride. Stirring was continued another hour. The yellow precipitate was vacuum filtered and washed with three 10-ml portions of a 5% hydrochloric acid solution, followed by three 10-ml portions of a water solution (pH 3.0). The complex was vacuum dried overnight over anhydrous calcium sulfate. There was obtained 0.67 g, 80% yield of yellow complex which melted with decomposition at 156 - 162°.

Analysis	Theory - %	Found
C	31.62	31.34
H	5.83	6.09
N	7.40	7.40
Cl	18.70	18.68
Pd	28.10	i) 27.9 ii) 27.6

Synthesis of Dichlorobis (di-n-propylketoxime-N,N')

palladium (II) -- $(C_7H_{15}NO)_2 \cdot PdCl_2$

A 50-ml solution of pH 3.0 containing 0.44 g of

anhydrous palladium (II) chloride was prepared exactly as previously outlined for the synthesis of the acetoxime and diethylketoxime complexes. To a 1:3 ethanol-water mixture totalling 100 ml, in a 250-ml beaker, 0.58 g di-n-propylketoxime was added. The pH was adjusted to 3.0 by the dropwise addition of a 10% potassium hydroxide solution. As previously outlined, the palladium (II) chloride solution was slowly added to the oxime solution. Precipitation of a yellow complex occurred within 2 minutes of the addition of the palladium (II) chloride solution. After the digestion period of one hour, the yellow complex was filtered, washed and dried exactly as outlined before. There was obtained 0.93 g of yellow complex, 94% yield, which melted at 134 - 138^o.

Analysis	Theory - %	Found
C	38.59	38.66
H	6.94	7.00
N	6.43	6.38
Cl	16.27	16.36
Pd	24.42	i) 24.20 ii) 24.42

Synthesis of Dichlorobis (di-n-butylketoxime-N,N')

palladium (II) -- $(C_9H_{19}NO)_2.PdCl_2$

A 50-ml solution at pH 3.0 of palladium (II) chloride was prepared as previously outlined and was added to a 50-ml, 2:1 ethanol-water mixture at pH 3.0 containing 0.71 g of di-n-butylketoxime. The pH adjustments of the reacting solutions to 3.0 and the addition of the palladium (II) chloride solution to the oxime solution were performed exactly as previously outlined. A yellow precipitate formed as the palladium (II) chloride solution was being added to the oxime solution. The normal one-hour digestion period with stirring was allowed. The yellow complex was filtered, washed and dried exactly as previously outlined. The resulting yellow complex weighing 1.08 g, 96% yield, melted at 105 - 108°.

Analysis	Theory - %	Found
C	43.96	43.78
H	7.78	7.87
N	5.70	5.66
Cl	14.42	14.38
Pd	21.64	i) 21.70 ii) 21.80

Synthesis of Dichlorobis (O-methylacetoxime-N,N') palladium

(II) -- $(C_4H_9NO)_2.PdCl_2$

To 0.78 g O-methylacetoxime (O-methylether), in a 250-ml beaker, was added 10 ml of 95% ethanol and 30 ml of water. The pH of the solution was adjusted to 3.0 by the dropwise addition of a 10% hydrochloric acid solution.

To 0.84 g of anhydrous palladium (II) chloride (10% excess), in a 250-ml beaker, was added 25 ml 6 N hydrochloric acid. The mixture was warmed gently on a hot plate until a clear, reddish-brown solution resulted. To this solution was added 50 ml of water and the pH was adjusted to 3.0 by the titrimetric addition of 6 N potassium hydroxide solution. The palladium (II) chloride solution was slowly added with continuous stirring to the O-methyl etherate solution. The pH of the mixture during and after addition of the palladium (II) chloride solution was monitored with a pH meter. A fine yellow precipitate formed within 15 minutes of complete addition of the palladium (II) chloride solution. Stirring was continued for another two hours and an overnight digestion period was allowed. The yellow crystals were vacuum filtered and washed with three 10-ml portions of a 5% hydrochloric acid solution followed by three 10-ml portions of a water solution (pH 3.0). The complex was vacuum dried overnight over anhydrous calcium

sulfate. The yellow complex weighing 0.47 g, 33% yield, melted at 124 - 126°.

Analysis	Theory - %	Found
C	27.33	27.40
H	5.16	5.40
N	7.97	7.79
Cl	20.17	20.01
Pd	30.26	i) 30.3 ii) 30.4

Synthesis of Dichlorobis (O-methyldiethylketoxime-N,N')

palladium (II) -- (C₆H₁₃NO)₂.PdCl₂

The palladium (II) chloride solution containing 0.84 g anhydrous palladium (II) chloride (10% excess) was prepared exactly as previously outlined for the synthesis of the O-methylether complex. To 1.024 g O-methyldiethylketoxime, in a 250-ml beaker, was added 15 ml of 95% ethanol and 35 ml of water. The pH of the solution was adjusted to 3.0 by the dropwise addition of a 10% hydrochloric acid solution. The palladium (II) chloride solution was slowly added to the etherate solution exactly as previously outlined. A fine yellow precipitate formed within 30 minutes of the complete addition of the palladium (II) chloride solution. Stirring was continued for another two

hours and an overnight digestion period allowed. The yellow crystals were vacuum filtered and washed with three 10-ml portions of a 5% hydrochloric acid solution followed by three 10-ml portions of a water solution (pH 3.0). The complex was vacuum dried overnight over anhydrous calcium sulfate. The yellow complex weighing 0.52 g, 35% yield, melted at 105 - 108^o.

Analysis	Theory - %	Found
C	35.36	35.31
H	6.43	6.33
N	6.87	6.93
Cl	17.39	17.16
Pd	26.10	i) 26.20 ii) 26.15

CHAPTER III

RESULTS

While the total infrared spectrum of a molecule can be used as its "fingerprint", being characteristic only of that compound, certain groups within a series of related molecules produce bands at frequencies which are characteristic of those groups regardless of the structure of the rest of the molecule (17).

There are two different types of vibrations of interest in the infrared region: stretching and bending. Stretching consists of movement along the bond axis such that interatomic distances increase and decrease. Bending consists of a change in bond angles between the bonds with a common atom or group of atoms.

The principal absorption peaks of prime importance in this study are those of the free oxime functional group (unbonded oxime), $C=N-OH$, the free etherate functional group (unbonded etherate), $C=N-OR$ where $R = CH_3$, and the bonded functional group of each oxime and etherate (coordination of the free functional group to a palladium (II) ion).

The infrared spectra of several oximes and O-methyl etherates as well as their corresponding palladium (II) complexes were examined in the 200 - 4000 cm^{-1} region. A comparison was made between the spectra of the free oxime and the etherate and that of the corresponding palladium complex to observe whether or not any frequency shifts had occurred for any particular absorption band. The presence of a shift in the stretching frequency of a particular absorption peak in the free ligand when compared to the same stretching frequency in the complexed ligand is a good indication that bonding occurs through the atom of that group (18).

BAND ASSIGNMENTS

The frequencies near 1300 cm^{-1} and 920 cm^{-1} are assigned to the OH deformation (bending), and N-O stretching modes, respectively. The absorption bands at approximately 1640 cm^{-1} and 3300 cm^{-1} are ascribed to C=N stretching and associated O-H stretching, respectively (19, 20). The associated O-H stretching arises from the intermolecular bonding between molecules of the oximes. A free distinct O-H band having a stretching frequency near 3600 cm^{-1} should be observed in the infrared spectrum (21) as well as the hydrogen bonded broad O-H stretching mode of the

associated O-H band near 3300 cm^{-1} .

The O-H bending band near 1300 cm^{-1} has a shift to 1265 cm^{-1} in solution spectra which is not unexpected since it has been noted in several instances that hydrogen bonding causes a frequency shift opposite to that occurring in the bands due to O-H stretching modes (22).

The principal bands for the C=N and N-O stretching modes of the O-methyl etherates should occur at approximately the same frequencies as the oxime. There is evidence in the literature for the assignment of the N-O stretching mode near 900 cm^{-1} (23, 24). Palm and Werbin (17) have assigned the N-O stretching frequency for oximes, O-methyl and N-methyl ethers near 940 cm^{-1} , since a strong band is observed in that region. In the same work, the C-O stretching frequency in the methoxy group of the methyl ethers was assigned at near 1050 cm^{-1} with a slight shift in going from solid to solution, analogous to the displacement of the N-O absorption bands in the oximes.

The additional bands of Pd-N and Pd-Cl found in palladium complexes usually occur near the 500 cm^{-1} and 340 cm^{-1} regions, respectively (25, 26, 27). However, the Pd-N stretching mode assignment is very approximate due to vibrational interferences of the ligand upon coordination (7).

The data obtained from the infrared spectral analysis

of the free oximes, free etherates and their corresponding complexes are listed in the following Tables.

TABLE I

INFRARED ABSORPTION BANDS FOR ACETOXIME
AND ITS PALLADIUM (II) CHLORIDE COMPLEX

Bond	Free Oxime	Complexed Oxime
C=N	1676 cm^{-1}	1668 cm^{-1}
N-O	940	1010
O-H (stretching)	3200 - 3400 broad	3210 narrow
O-H (deformation)	1265	1278
Pd-Cl		330
Pd-N		not resolvable

TABLE II

INFRARED ABSORPTION BANDS FOR DIETHYLKETOXIME
AND ITS PALLADIUM (II) CHLORIDE COMPLEX

Bond	Free Oxime	Complexed Oxime
C=N	1662 cm^{-1}	1668 cm^{-1}
N-O	930	1015
O-H (stretching)	3300 - 3200 broad	3220 - 3200 narrow
O-H (deformation)	1255	1250
Pd-Cl		348
Pd-N		not resolvable

TABLE III

INFRARED ABSORPTION BANDS FOR
DI-n-PROPYLKETOXIME AND ITS PALLADIUM (II)

CHLORIDE COMPLEX

Bond	Free Oxime	Complexed Oxime
C=N	1662 cm ⁻¹	1665 cm ⁻¹
N-O	970	1010
O-H (stretching)	3350 - 3200 broad	3310 narrow
O-H (deformation)	1240	1230
Pd-Cl		360
Pd-N		not resolvable

TABLE IV
INFRARED ABSORPTION BANDS FOR
DI-n-BUTYLKETOXIME AND ITS PALLADIUM (II)
CHLORIDE COMPLEX

Bond	Free Oxime	Complexed Oxime
C=N	1662 cm^{-1}	1665 cm^{-1}
N-O	960	1020
O-H (stretching)	3300 broad	3300 narrow
O-H (deformation)	1240	1235
Pd-Cl		355
Pd-N		not resolvable

TABLE V
INFRARED ABSORPTION BANDS FOR
O-METHYLACETOXIME AND ITS PALLADIUM (II)
CHLORIDE COMPLEX

Bond	Free Etherate	Complexed Etherate
C=N	1640 and 1660 cm^{-1}	1650 cm^{-1}
N-O	890	940
O-CH ₃	1050	1040
Pd-Cl		350
Pd-N		not resolvable

TABLE VI

INFRARED ABSORPTION BANDS FOR
O-METHYLDIETHYLKETOXIME AND ITS PALLADIUM (II)

CHLORIDE COMPLEX

Bond	Free Etherate	Complexed Etherate
C=N	1630 cm ⁻¹	1630 cm ⁻¹
N-O	880	920
O-CH ₃	1060	1050
Pd-Cl		350
Pd-N		not resolvable

CHAPTER IV

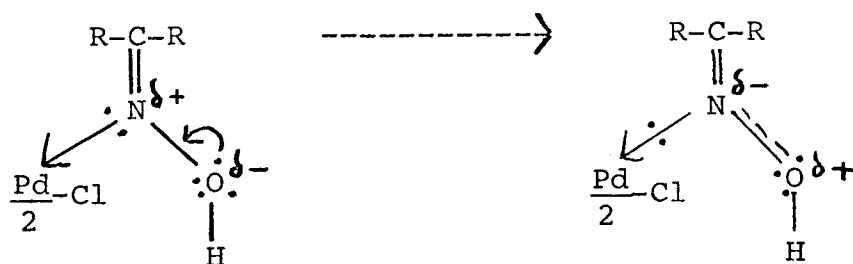
DISCUSSION

The oximes, etherates and their corresponding palladium (II) chloride complexes have been prepared as previously outlined. The purity and identification of the compounds is as described earlier. The data obtained for the frequencies of the principal absorption bands of complexed ligand and free ligand are summarized in Tables I through VI.

According to the spectral data obtained, the most significant feature revealed is the increase in the stretching frequency of the N-O stretching mode in going from free ligand to complexed ligand.

In the free oximes, strong bands occurred in the 930 to 960 cm^{-1} region and these were assigned to the N-O stretching frequency of the oximes. Similar intense bands in the complexed oximes occurred in the 1010 to 1020 cm^{-1} region, and these were attributed to the N-O stretching modes of the complexed oximes. This represents a frequency shift of approximately 40 to 90 cm^{-1} when comparing individual free oximes to their corresponding complexes. An increased frequency is indicative of an

increase in the bond strength (28). The increased strength of the N-O bond in the coordinated oxime could be due to the donation of electrons from the oxygen atom into the N-O bond increasing the π character (electron density) of the bond. The electrons from the oxygen atom enter the N-O bond so as to decrease the slight positive character that the nitrogen atom attains when forming a coordinate covalent bond during complexation of the palladium (II) chloride molecule by donation of its unpaired electrons. The phenomena schematically could be illustrated as follows:

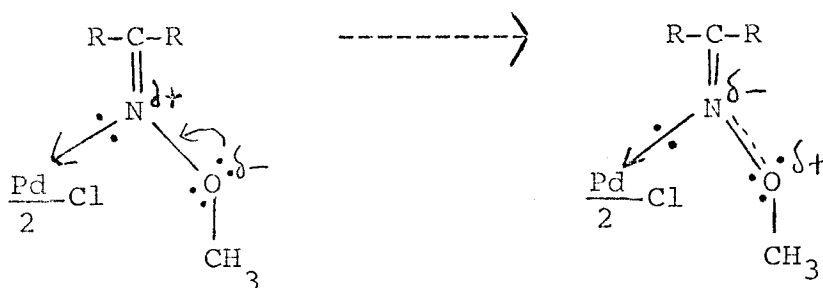


The above rearrangement of electrons could explain why a drop in pH (liberation of hydrogen ion) occurred during coordination of the free oxime ligand to the palladium (II) chloride.

The free etherate ligands showed intense bands in the 880 to 890 cm^{-1} region and these were assigned to the N-O stretching mode of the O-methyl ethers. A similar band was found in the complexed etherates in the 920 to 940 cm^{-1} region indicating an increased vibrational

frequency shift (upshift).

The same explanation of the electrons being donated from the oxygen atom into the N-O bond that is suggested for the oximes can be applied here to etherates. Schematically it can be illustrated:



Medium bands appearing in the 1680 to 1660 cm^{-1} spectrum region of the oximes were assigned to the C=N stretching frequency mode of the free unbonded oxime group.

Similar characteristic bands appeared in the 1670 to 1660 cm^{-1} spectral region of the complexed oximes and these were attributed to the C=N stretching modes of the palladium oxime complexes.

Since the location of the C=N absorption peaks of the free oximes and complexed oximes is in the same region, coordination seems to have little effect on the C=N stretching frequency. It was expected that coordination of the palladium (II) chloride to the nitrogen donor atoms of the ligand would cause a downshift (decrease in vibrational frequency of the C=N band) in the stretching

frequency of the C=N absorption band. However, no significant shift in the stretching frequencies could be established between the free oxime ligand and its complex. This lack of shift may be attributed to high electron density or π character of the carbon to nitrogen double bond.

The weak to medium bands appearing in the 1630 to 1660 cm^{-1} spectrum region were assigned to the C=N stretching mode of the free O-methyl ether functional group. In the complexed etherates, similar bands occurred in the 1630 to 1650 cm^{-1} region, again showing no significant frequency shift.

The presence of two C=N stretching modes in O-methylacetoxime is surprising, particularly as shown in the infrared spectrum of the O-methylacetoxime which revealed two C=N stretching bands, one occurring at 1640 cm^{-1} and one at 1660 cm^{-1} , both being weak to medium in intensity. It appears that some sort of splitting in the C=N band takes place.

In the spectrum of the O-methylacetoxime palladium (II) complex, only one C=N stretching band occurring at 1650 cm^{-1} could be found, thus it seems that when coordination takes place, the splitting disappears. No attempt will be made to explain the above phenomena, other than to state

that it could be an inherent characteristic of the structure of the O-methylacetoxime molecule.

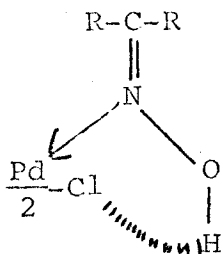
Also of importance in the spectrum of the functional groups of the oxime were the free O-N stretching modes, associated O-H stretching modes and the O-H deformation modes of the free and complexed oximes. Of similar importance was the O-CH₃ stretching mode of the free etherate and the complexed etherate.

In the free oxime, broad intense bands occurred in the 3400 to 3200 cm⁻¹ region. These were characteristic of the associated O-H stretching modes of the free oximes. In the complexed oximes, similar characteristic bands, but not as broad, were found in the 3200 to 3300 cm⁻¹ region and these were assigned to the associated (hydrogen bonded) O-H stretching mode of the oxime palladium (II) complex.

A medium band characteristic of free O-H stretching was found around 3600 cm⁻¹ in the spectrum of the free oximes. In the complexed oximes this band of free O-H stretching disappeared.

This is indicative of hydrogen bonding which could occur between the labile hydrogen of the oxime functional group and the chloride atom of the palladium (II) chloride molecule during coordination. An illustration is shown

below:



This hypothesis also explains the drop in pH from 3.0 to 2.5 during coordination of the oximes with the palladium (II) chloride.

The medium intensity bands occurring between 1265 and 1240 cm^{-1} in the free oximes were attributed to the O-H deformation mode of the free oxime functional group since these bands were representative of the O-H deformation band in oximes. Comparable bands were located in the 1278 to 1235 cm^{-1} region of the complexed oximes. No significant change (shift) in the bending mode of the O-H bond could be detected in going from free oxime to complexed oxime; consequently, coordination seems to have little effect on the bending mode of the O-H bond.

In the free etherates, strong intense bands were located in the 1050 to 1060 cm^{-1} spectral region of the free etherates. These bands are characteristic and representative of the O-CH₃ stretching frequency of the etherate functional group (22). Coordination with palladium (II) chloride seems to have little effect on the O-CH₃ stretching

frequency, since similar bands were found in the 1040 to 1050 cm^{-1} region of the complexed etherates. Thus, no significant change occurred in the O-CH₃ band in going from the free etherate to the complexed etherate.

It is important to note that in the complexed oximes and etherates, Pd-Cl and Pd-N bands should be visible in the infrared region. The spectrum of a reference compound, diamminedichloropalladium (II) -- $\text{Pd}(\text{NH}_3)_2\text{Cl}_2$ (Research Inorganics) -- was obtained. A weak absorption peak was observed at 499 cm^{-1} and a medium to strong peak at 340 cm^{-1} . The peak at 499 cm^{-1} was assigned to Pd-N which is in accordance with the literature (25). The peak at 340 cm^{-1} was assigned to the Pd-Cl stretching frequency (26).

In the palladium (II) complexes of the oximes and etherates, peaks were found in the 330 to 370 cm^{-1} region and these were attributed to the Pd-Cl stretching modes of the complexes.

No peak which could be unequivocally assigned to Pd-N stretching was found around the 500 cm^{-1} region for the complexes. Possible reasons for the indistinguishable Pd-N vibrational frequency are the weakness of the Pd-N band and interferences arising from ligand vibrations which are activated by coordination or complex formation,

the symmetry of the molecules and intermolecular interactions (7).

CHAPTER V

SUMMARY AND CONCLUSIONS

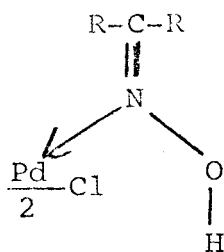
A series of coordination compounds of palladium (II) chloride were prepared using the oximes and the etherates as ligands.

The complexes formed were all yellow crystalline solids having, in most instances, a melting point below 200° . A few melted with decomposition. The complexes were all soluble and stable in chloroform with the exception of the acetoxime complex which had a limited solubility.

Generally, the oximes and the etherates reacted with bivalent palladium to form stable complexes. The formation of the oxime and the etherate palladium complexes were carried out at a pH 3.0.

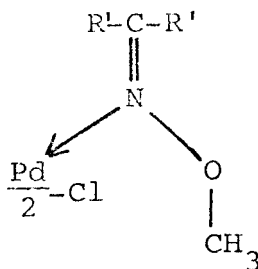
It was found that the ligand to metal ratio for complex formation was 2:1. The proposed structures of the oxime and etherate complexes are listed on the following page:

Oxime Complex



where R = CH₃, C₂H₅, C₃H₇
and C₄H₉.

Etherate Complex



where R' = CH₃ and C₂H₅

The proposed structures are based on elemental analysis, the course of the reactions and infrared spectral analysis.

From the evidence obtained, it is reasonable to conclude that the oxime and etherate ligands bond to bivalent palladium through the nitrogen donor atom.

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