

The University of Manitoba

THERMOGRAVIMETRIC ANALYSIS AND
MASS SPECTRAL STUDIES OF SOME
TRANSITION METAL VIC - DIOXIMATES

by

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A Thesis

Submitted to

the Faculty of Graduate Studies and Research

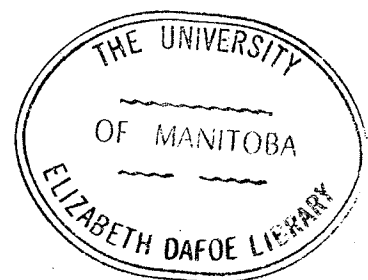
In Partial Fulfilment

of the Requirements for the Degree

MASTER OF SCIENCE

Winnipeg, Manitoba

December, 1969



ACKNOWLEDGEMENT

I owe my deepest appreciation to my Supervisor, Dr. J. B. Westmore for his patience and careful guidance throughout the whole course of this work. I also have to thank Dr. C. Reichert and Mr. D. Lin for their help and suggestions.

Without the care and thoughtfulness of the Pollard's family my study and stay in Canada would have been less valuable and my gratitude to them cannot be expressed in words. Special thanks are also due to Miss Winnie Chan for the encouragement and for her help in the typing.

I am also grateful to all my friends and to the whole Chemistry Department for providing me with such immense opportunity and tremendous experience. I also would like to express my thanks to Miss D. Ostlere and Mr. T. Kiezer and Mr. L. Krucynski for helping me with the pictures and spectra.

To My Parents and Brother

ABSTRACT

The Ni(II), Pd(II) and Pt(II) complexes of dimethylglyoxime, diphenylglyoxime, α -furildioxime, nioxime and 4-methylnioxime have been studied by thermoanalytical and mass spectrometric means.

It is found that the decompositions of the vic-dioximates are affected by the presence of oxygen and that these decompositions are exothermic. All of the complexes are stable up to 250°C with the platinum complexes decomposing at the lowest temperatures, contrary to the general thermal stabilities of square planar complexes of this group of metals.

Mass spectra of the complexes were recorded with an electron energy of 50 volts and they show fair degrees of complexity, especially the nioxime and 4-methyl-nioxime complexes where decomposition of the cyclohexane ring also took place. General trends between the various metals and ligands are not clearly shown but participation through π -bonding of the metal p_z orbital in the stabilization of the ion is suggested. This participation might be expected to increase as the ease of oxidation of the metal increases, i. e. $\text{Ni} < \text{Pd} \approx \text{Pt}$ so that the relative intensities of the $(\text{P} - \text{OH})^+$ and $(\text{P} - \text{R})^+$ ions should be in the sequence $\text{Ni} > \text{Pd} \approx \text{Pt}$. In fact, the opposite trend was found. This may be attributed to many factors among which atomic size of the metals and their relative ionization potentials might be important.

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CHAPTER ONE
GENERAL SURVEY
OF
LITERATURE WORK

Nickel, palladium and platinum vic-dioximates (1), especially those formed from dimethylglyoxime have been much studied by X-ray (2 - 8), infra-red (9), ultra-violet and visible (10, 11) spectroscopy. Their nucleation and generation (12, 13) and effects of pressure on them (14) have also been investigated. The tremendous amount of attention given to this group of inner-metallic complex salts (15) has been due to their low solubility and thus their use as gravimetric determination and / or separation reagents for nickel, palladium and platinum. (16, 17, 18) It is hoped that the study of the thermograms and mass spectra of some of these complexes will give a more thorough understanding of this particular group of compounds. We have made the study of the nickel, palladium and platinum complexes formed from the following dioximes (table I) :

1. Dimethylglyoxime
2. Diphenylglyoxime
3. α -furildioxime
4. Nioxime
5. 4-Methyl-nioxime

It has been concluded (3) that most of these complexes have similar crystal structures. The metal-nitrogen (ligand) distances are characteristic of each metal, being similar to the metal-nitrogen (oxime) distances of other mono- or di- oxime complexes and shorter than the metal-nitrogen (amine) bond distances in the amine complexes. (See table II for comparison). The O-H-O bond distances are short

TABLE I. COMPLEXES STUDIED AND ABBREVIATION USED

M = Nickel, palladium and platinum (II)

OXIMES	$R-C(=N-OH)-C(=N-OH)-R$	FORMULA	STRUCTURE OF COMPLEX	ABBR. USED
Dimethylglyoxime		R = CH ₃		M(DMG) ₂
Diphenylglyoxime (benzildioxime)		R = Ph		M(DPG) ₂
α -furildioxime		R =		M(α -DFD) ₂
OXIMES				
Nioxime		R = H		M(Niox) ₂
4-Methyl-Nioxime		R = CH ₃		M(4MNiox) ₂

TABLE II. BOND LENGTHS AND BOND ANGLES IN THE METAL VIC-DIOXIMATES AND RELATED COMPOUNDS

SPECIFICATIONS AND ABBREVIATIONS:

Bond angles are in A

EMG = ethylmethylglyoxime

C - C = C - C bond distance between the dioxime groups

NiAO = Bis(2-amino-2-methyl-3-butanone-oximato) nickel(II) chloride monohydrate

Ni(SAD)₂ = salicylaldoxime-Ni(II)

a = J. R. Wiesner and E. C. Lingafelter, Inorg. Chem. 5, 1770 (1966)

b = R. Shintain, Acta Cryst, 13, 609 (1960)

c = Intramolecular Distances, 18, London Chem. Soc. 1965

HB = Handbook of Chemistry and Physics, 46th Edition

Compound	M-N distance		O-H-O distance	MNO bond angle		N-C distance		NCC bond angle		C-C	Ref.
Ni(DMG) ₂	1.90	1.87	2.44	118	122	1.20	1.25	109	113	1.53	2, 7, 8
Pd(DMG) ₂	1.93	1.99	2.59 - 2.62	-	-	1.31	1.31	-	-	1.47	3, 8
Pt(DMG) ₂	1.93	1.95	3.03	134	135	1.27	1.38	117	113	1.57	2
Cu(DMG) ₂	1.93	1.96	2.53 - 2.70	121.5	125	1.22	1.27	114	110.5	1.53	3, 5, 8
NiAO	1.85	1.91	2.38	121.5	-	1.30	1.52	114	106	1.50	3
Ni(SAD) ₂	1.86	-	2.52	122	-	1.40	1.40	-	-	-	c
Ni(en) ₃ (NO ₃) ₂	2.12	-	-	-	-	1.50	1.50	111	-	1.50	a
Pd(en) ₂ Cl ₂	2.04	2.03	-	-	-	1.47	1.48	107	-	1.51	a
Pt(SN) ₄	2.15	2.03	-	-	-	-	-	-	-	-	c
K ₄ (Ni(NO ₂) ₆)	2.15	-	-	-	-	-	-	-	-	-	c
K ₂ Pd(NO ₂) ₄	2.10	-	-	117	-	-	-	-	-	-	c
K ₂ Pt(NO ₂) ₄	2.02	-	-	-	-	-	-	-	-	-	c
DMG	-	-	-	-	-	1.27	1.27	115	-	1.44	c
Ethane	-	-	-	-	-	-	-	-	-	1.54	HB
Ethylene	-	-	-	-	-	-	-	-	-	1.34	HB
Benzene	-	-	-	-	-	-	-	-	-	1.39 ₅	HB

TABLE II. BOND LENGTHS AND BOND ANGLES (cont'd)

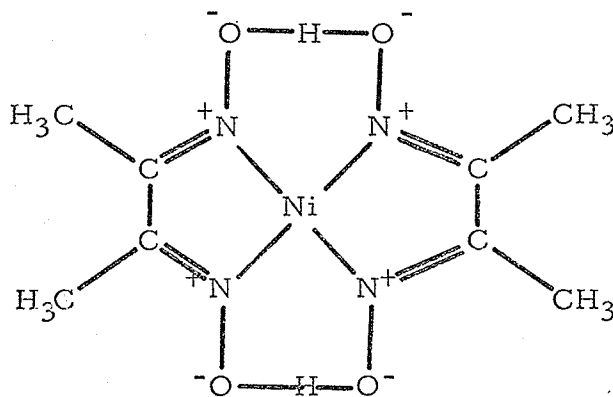
Compound	M-N distance	O-H-O distance	MNO bond angle	N-C distance	NCC bond angle	C-C	Ref.
Acetylene	-	-	-	-	-	1.20	HB
β -diketone	-	-	-	-	-	1.49	HB
Paraffin							
4 coval. N	-	-	-	1.48	-	-	HB
3 coval. N	-	-	-	1.47	-	-	HB
Partial double bond: $(\text{HNC}=\text{O})_2$	-	-	-	1.32	-	-	b
Pyridine	-	-	-	1.35	-	-	b
Triple bond	-	-	-	1.16	-	-	b

and increase from the nickel to the palladium and platinum complexes; and none of these compounds have been conclusively shown to have symmetrical hydrogen bonds ($\nu_{\text{OH}} = 2300 - 2900$) (19), although the oxygen-oxygen bond distance in $\text{Ni}(\text{DMG})_2$ is short enough to suggest the existence of a single-minimum potential energy well. (3, 6, 19) Also this hydrogen on the bond is difficult to be replaced. The importance of metal-metal intermolecular interactions in the symmetrical planar complexes of nickel, palladium and platinum dimethylglyoximates (and even the heptoximates which are much less symmetrical) has been the subject of much dispute. Through X-ray (20), solubility (16, 21, 22) and dichroism (23) studies, Yamada and Tsuchida, Banks and Caton, Banks and Barnum, Godycki and Rundle had been able to say that metal-metal bonds do exist, with magnitudes of about 10 kcal / mole. (23) However, in more recent work, Basu, Cook and Belford (11), Anex and Krist (10) argued that the observed "abnormal" dichroism and comparatively low solubility of these compounds (which were taken as evidence for metal-metal bonding) might well be due to normal vibronic selection rules in a centric molecule and to crystal packing. Ingraham (24) undertook a theoretical molecular orbital treatment of nickel dimethylglyoximate using the extended Wolfsberg-Helmoltz method. He concluded that there is no evidence of metal-metal interaction in the ground state, but such interaction could happen in the excited states. The latest information obtainable was given by Thomas,

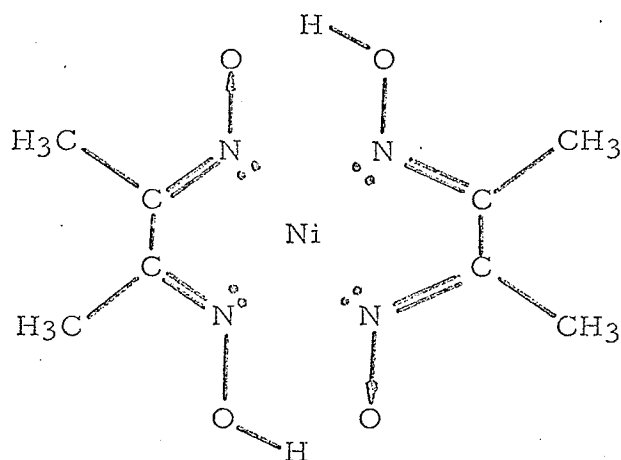
Underhill (25) and Bhat, Chaudrashekhar and Rao (26). Through a vibrating reed electrometer, they were able to detect semi-conductivity from these complexes ($6.3 \times 10^{-15} \text{ ohm}^{-1} \text{ cm}^{-1}$ for $\text{Ni}(\text{DMG})_2$ and $8.9 \times 10^{-12} \text{ ohm}^{-1} \text{ cm}^{-1}$ for $\text{Pd}(\text{DMG})_2$, both at 100°C). And Thomas and Underhill claimed their measurements to be the first direct evidence for electron delocalization along the line of metal-metal stacking. No evidence of metal-metal bonding would be expected from mass spectral studies since the high energy of electron impact will be too great to preserve this weak bond, if it ever existed. As can be seen from table II, complexing the metal with the vic-dioximes in every instance results in formation of rather strong metal-nitrogen bonds, as evidenced by the short bond lengths (1.85 \AA for $\text{Ni}(\text{DMG})_2$ and 1.96 \AA in $\text{Pt}(\text{DMG})_2$ as compared to 2.12 \AA in triethylenediamine-Ni(II)-nitrate, $\text{Ni}(\text{en})_3(\text{NO}_3)_2$). Also the C-C bond between the dioxime (NOH) groups is increased from 1.44 \AA in the free ligand to $1.50 \pm 0.03 \text{ \AA}$ in the complexes, reflecting probably a "pull-over" of the little double bond character of the carbon-carbon bond through the carbon-nitrogen bonds to the metal-nitrogen bonds. Complexation decreases the carbon-nitrogen bond length in the case of nickel dimethylglyoximate ($1.27 \text{ \AA} \longrightarrow 1.23 \text{ \AA}$) and increases it in the case of palladium and platinum dimethylglyoximates ($1.27 \text{ \AA} \longrightarrow 1.31 \text{ \AA}$ and 1.38 \AA respectively.) The C-C bond ($1.47 - 1.57 \text{ \AA}$) is longer than the aromatic C-C bond (1.395 \AA in copper acetylacetonate, 1.404 \AA in benzene) and encompasses

that of a normal C-C single bond ($1.54 \overset{\circ}{\text{A}}$ in ethane). Thus, there appears to be some conjugation through the metal-nitrogen-carbon bonds to give each of these bonds some double-bond character, but the C-C bond seems to have little double-bond character. This was postulated by Godycki and Rundle from their X-ray studies and supported by Banks and Barnum (22) through their studies of the absorption spectra of some of these vic-dioximates. Additional maxima at 435 μ and 406 μ (for $\text{Ni}(\alpha\text{-DFD})_2$ and $\text{Ni}(\text{DPG})_2$ respectively) were observed with respect to those observed for $\text{Ni}(\text{Niox})_2$, $\text{Ni}(4\text{MNiox})_2$, $\text{Ni}(\text{DMG})_2$ and nickel heptoximate. They attributed these additional peaks to conjugation of the vic-dioxime groups with the aromatic groups. They found a similar effect with the palladium complexes.

The molecular structure given by Godycki and Rundle (7) is



with a symmetry which may be as high as D_{2h} . The four positive charges lie on the nitrogen atoms, and are neutralized by the oxygen atoms. Hückel preferred the following form :



This would also give the nickel atom a very strong stable electronic configuration and ensure four very strong M-N bonds. In view of the five electrons present in the electron-donor nitrogen atom, covalency seems to be rather appropriate for the M-N bonds. This nature of covalency for the M-N bonds had been proposed by Banks (21) for $Ni(DMG)_2$ from his charge transfer absorption spectra studies. However, there is still a lack of knowledge as to how the metal and ligand orbitals are mixed when we consider the problem from the molecular orbital calculation point of view. (10)

From the mass spectral study of these complexes, it is hoped that a little more about the bonding can be said.

CHAPTER TWO
THERMOGRAVIMETRIC ANALYSIS

SECTION I. INTRODUCTION

Thermogravimetric analysis (TGA) together with other techniques such as differential thermal analysis (DTA) and gas evolution detection (GE or GED) are not new thermoanalytical methods, but it is only in recent years have they become highly developed research tools. TGA has been employed in the studies of such various physicochemical aspects such as thermal stability temperatures, dissociation intermediates, thermal stability of intermediates, residue composition and kinetics. (28) And Honda (29), Newkirk (30, 31), Duval (32) and Wendlandt (33) have been especially noted for their contribution to this field. However, the literature concerning thermal analysis contains many contradictions and anomalies. The shape of a thermogram can depend on so many factors such as sample size, state of subdivision, how tightly the sample is packed in its container, shape of the container, rate of heating, ambient atmosphere and detection device. (31) Other effects like thermo-molecular flow, aerodynamics and temperature coefficient can be important too, especially when the experiment is carried out in vacuum. The thermogram of calcium oxalate, for example, has often been used as a standard for thermobalance operation yet it has been shown that the shape of the thermogram is dependent on so many of these factors. The effect of some of these variables is greater with large samples than with small samples. Commonly samples as large as 0.5 - 1.0 gram have been used in the

recent past. The highly sensitive Cahn balance used here allowed reproducible results to be obtained with samples as small as 1mg. For these small samples, the effect of temperature gradients within the sample should be minimal but many of these other variables can still be operative.

The thermolysis of some of the vic-dioximates was first studied by Duval (32) but with the advent of new highly developed thermobalances, a renewed study of them is necessary. The thermal stability of them has to be known first before the interpretations of their mass spectra are justified.

SECTION II. INSTRUMENTAL - THE THERMAL BALANCE

The thermal balance used here is the Perkin - Elmer TGS - 1 model (fig 1). The main components are shown alongside the diagram. It provides a record of microgram level weight changes in the sample as a function of temperature while it is being heated. The temperature is controlled through a temperature programmer in a differential scanning calorimeter (Perkin - Elmer DSC - 1 B type) connected to the TGA - 1. The main components are described in the following. (34)

(a) The Cahn RG Automatic Electrobalance works on the null-balance principle. (35) A change in weight of the sample in the sample pan in loop A (or loop B) will cause a deflection of the beam. The flag at the end of the beam will move with it, changing the light

FIG. 1

THERMOBALANCE COMPONENTS
OF MODEL TGS-1