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PART ONE: PYRIDINE COMPLEXES OF ZINC(II), CADMIUM(II), AND MERCURY(II) NITRATES PART TWO: PRELIMINARY INVESTIGATION OF SOME OXIDATION AND COMPLEXATION REACTIONS OF GROUP V-B METALS IN NONAQUEOUS SOLVENTS

THOMAS JAMES OUELLETTE

PART ONE

PYRIDINE COMPLEXES OF ZINC(II), CADMIUM(II),

AND MERCURY(II) NITRATES

PART TWO

PRELIMINARY INVESTIGATION OF SOME OXIDATION AND COMPLEXATION

REACTIONS OF GROUP V-B METALS IN NONAQUEOUS SOLVENTS

BY

THOMAS JAMES OUELLETTE

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ABSTRACT

PART ONE

PYRIDINE COMPLEXES OF ZINC(II), CADMIUM(II), AND MERCURY(II) NITRATES

PART TWO

PRELIMINARY INVESTIGATION OF SOME OXIDATION AND COMPLEXATION REACTIONS OF GROUP V-B METALS IN NONAQUEOUS SOLVENTS

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This thesis is divided into two parts. Part I deals with pyridine complexes of zinc(II), cadmium(II), and mercury(II), which were prepared by the reaction of the anhydrous metal nitrates with pyridine in nonaqueous solution. Additional pyridine-nitrate complexes of the group II-B metal nitrates were synthesized by thermal decomposition reactions. The complexes which were characterized in this study include: $[Zn(py)_3(NO_3)_2]$, $[Zn(py)_2(NO_3)_2]$, $[Zn(py)_3(NO_3)_2] \cdot 3py$, $[Cd(py)_3(NO_3)_2]$, $[Cd_2(py)_3(NO_3)_4]$, $[Cd(py)_3(NO_3)_2] \cdot 3py$, $[Hg(py)_2(NO_3)_2]$, and $[Hg(py)_2(NO_3)_2] \cdot 3py$. Characterization of the complexes by means of dta, tga, conductance, magnetic susceptibility, molecular weight, X-ray diffraction, ultraviolet and visible spectroscopy, and regular and far-infrared spectroscopy led to tentative structural assignments. It was concluded that the tris(pyridine) complex of zinc(II) had a

trigonal bipyramidal or distorted octahedral geometry, that the bis(pyridine) complexes of zinc(II) and mercury(II) had a pseudotetrahedral geometry, that the tris(pyridine) and tetranitrato complexes of cadmium(II) had a polymeric distorted octahedral geometry, and that the three trisolvates had a geometry analogous to their parent complexes, but with an additional three moles of crystal pyridine.

Part II of this thesis deals with a study of the oxidation of the group V-B metals by silver nitrate and bromine in nonaqueous solvents, and complexing of the oxidized metals with ammonium fluoride and pyridine. It was found that the group V-B metals could be oxidized in 1,2-dimethoxyethane, dioxane, and formamide, and in many cases ammonium fluoride and pyridine complexes could be isolated. The oxidation reactions were generally complicated by solvent interaction, and the complexes obtained from the oxidized metal solutions were mostly mixtures, which could not be adequately purified.

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Thomas G. Ouellette

THIS THESIS IS DEDICATED TO MY PARENTS.

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PART ONE

PYRIDINE COMPLEXES OF ZINC(II), CADMIUM(II),

AND MERCURY(II) NITRATES

I. INTRODUCTION

Pyridine complexes of the transition and post-transition metals have been studied in great detail by a large number of workers.[1-16] Two somewhat unique characteristics of pyridine complexes are the exhibition of a wide variation in thermal stability,[15] and the preparation of more than one pyridine complex from the same metal salt.[17] Surprisingly, very little work has been reported on complexes of anhydrous metal nitrates.[18-31] In this work, the results of studies on the pyridine complexes of anhydrous metal nitrates of zinc(II), cadmium(II), and mercury(II) are reported.

In designing this problem there were basically two primary objectives. The first of these was to ascertain which pyridine complexes of zinc(II), cadmium(II), and mercury(II) could be prepared. Grossman[32] has reported the synthesis of $Zn(py)_2(NO_3)_2 \cdot 2H_2O$ and $Cd(py)_2(NO_3)_2 \cdot 2H_2O$, but the only anhydrous pyridine-nitrate complexes of the group II-B metals which have been reported are $Zn(py)_3(NO_3)_2$[11] and $Hg(py)_2(NO_3)_2$,[31] and in both cases only meager information was given on these compounds.

The second objective in this project was to study the physical and chemical properties of the pyridine-nitrate complexes of the group II-B metals with the emphasis directed toward elucidating their stereochemical properties. The geometries of a large number of zinc(II), cadmium(II) and mercury-(II) complexes have been previously investigated, and exhibit considerable variety. Zinc(II) complexes are most commonly

tetrahedral or pseudotetrahedral, but complexes exhibiting other geometries are frequently encountered.[13,34] Cadmium(II) complexes are generally octahedral, but once again numerous other geometries have also been observed.[7,20] Mercury(II) complexes seem to favor tetrahedral and octahedral geometries, and frequently polymeric complexes with both of these geometries are found.[13,16]

Since this study encompasses nitrate complexes, different types of coordinate bonding are possible. Nitrate groups can function as ionic, monodentate, bidentate, and bridging ligands.[34,36]

The synthetic and structural aspects in this work required the use of differential thermal analysis, thermogravimetric analysis, mass spectrometry, molecular weight measurements, magnetic measurements, X-ray powder diffraction measurements, infrared spectroscopy, conductivity measurements, ultraviolet-visible spectroscopy, and far-infrared spectroscopy.

Part I of this thesis is divided into four major sections. Section I is the introduction, and includes a brief discussion of the purpose and scope of this work. Section II consists of the experimental aspects of this work, giving a detailed description of the synthesis and experimental techniques used in characterizing the complexes. Section III presents the results of the work, and a discussion of the conclusions. Section IV summarizes briefly the results of this investigation. Following Section IV is a list of references.

II.   EXPERIMENTAL

A.   Starting Materials.

Reagent grade methanol (Fisher) was dried by distillation from magnesium activated with iodine. Reagent grade pyridine (Fisher) was dried by distillation from potassium hydroxide pellets and stored over barium oxide until used. Practical grade 2,2'-dimethoxypropane (Eastman) was used without further purification. All other chemicals were of reagent grade and include: anhydrous diethyl ether (Fisher), N,N'-dimethylformamide (Eastman), chloroform (Fisher), silver nitrate (Fisher), bismuth (J. T. Baker, powder), zinc (J. T. Baker, 20 mesh), cadmium (Fisher, mossy, sticks), zinc(II) nitrate hexahydrate (Fisher), cadmium(II) nitrate tetrahydrate (Fisher), mercury(II) nitrate monohydrate (Fisher), and mercury(II) oxide (Fisher, yellow), which were used without further purification.

B.   Preparation of the Zinc Complexes.

Precursors to the synthesis of some of the complexes were the differential thermal analysis (dta) and thermogravimetric analysis (tga) of dinitratotris(pyridine)zinc(II). An outline of this work is found in subsections F and G.

1.   Preparation of Dinitratotris(pyridine)zinc(II), $[Zn(py)_3(NO_3)_2]$, from Zinc Metal.
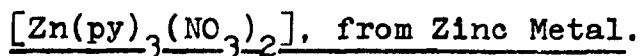
Granular zinc (7.5 g, 0.15 mole) was added to a magnetically stirred solution of 34 g (0.21 mole) of silver nitrate in 100 ml of dry methanol. For the first hour the

mixture was cooled in an ice bath because the reaction was highly exothermic. After stirring for a total of 32 hr, the mixture gave a negative test for the presence of Ag^+, using 6 M hydrochloric acid. The reaction mixture was filtered to remove suspended solids, and 25 ml (0.32 mole) of dry pyridine was added to the warm filtrate. The solution was concentrated over an infrared lamp to a final volume of 40 ml and placed in a refrigerator at $0°$ to induce crystallization. At the end of 12 hr a copious amount of white crystalline material was present in the flask. The product was collected on a sintered-glass filter and washed twice with dry methanol followed by two washings with anhydrous ether. The product was recrystallized by dissolving it in a minimal amount of boiling methanol to which was added 10 ml of pyridine. After standing for 12 hr at room temperature, the mixture was filtered through a sintered-glass filter and the solid was washed successively with two 20-ml portions of methanol and two 20-ml portions of anhydrous ether. The compound was freed of remaining solvent by storage in an evacuated desiccator over silica gel for 6 hr.

Anal. Calcd for $[Zn(py)_3(NO_3)_2]$: Zn, 15.32; N, 16.42; C, 42.22; H, 3.54. Found: Zn, 15.53; N, 16.53; C, 41.76; H, 3.47.

2. Preparation of Dinitratotris(pyridine)zinc(II), $[Zn(py)_3(NO_3)_2]$, from Zinc(II) Nitrate Hexahydrate.

Zinc(II) nitrate hexahydrate (29.8 g, 0.110 mole) was added to 100 ml of 2,2'-dimethoxypropane in a 250-ml single-necked, round-bottomed flask fitted with a reflux condenser.

The mixture was refluxed for 14 hr, yielding a pale yellow solution. The condenser was removed and the boiling continued to a final volume of 40 ml. The reaction mixture was filtered to remove any suspended solids, and 24 ml (0.31 mole) of dry pyridine was added to the warm filtrate. No immediate precipitation occurred, but after standing for 24 hr at room temperature a large quantity of transparent, crystalline material was present in the flask. The product was collected on a sintered-glass filter and washed with anhydrous ether. The product was recrystallized by dissolving it in a minimal amount of methanol to which was then added 10 ml of pyridine. After standing at room temperature for 18 hr, transparent crystals had formed in the flask. The product was collected on a sintered-glass filter and washed successively with two 20-ml portions of methanol and two 20-ml portions of anhydrous ether. The product was finally dried for 6 hr in an evacuated desiccator over silica gel.

Anal. Calcd for $[Zn(py)_3(NO_3)_2]$: Zn, 15.32; N, 16.42; C, 42.22; H, 3.54. Found: Zn, 15.54; N, 16.41; C, 42.12; H, 3.43.

3. **Preparation of Dinitratobis(pyridine)zinc(II),** $[Zn(py)_2(NO_3)_2]$.
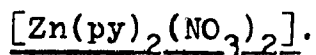
A weighed sample of dinitratotris(pyridine)zinc(II) was finely ground and placed in a porcelain crucible. The crucible was placed in a Hoskins combustion furnace, which was heated to 115° and through which a slow stream of dry nitrogen gas was passed. The sample was removed from the furnace, weighed, and reground several times over a period of

9.5 hr. At the end of this time no further change in weight was observed. The sample had lost 18.83% of its original weight, which compares favorably with a theoretical weight loss of 18.54% for the formation of the bis(pyridine) complex. The final product was a very pale pink solid; the total change in weight, therefore, corresponded to the loss of one mole of pyridine per mole of starting material. The reaction is therefore:

$$[Zn(py)_3(NO_3)_2] \xrightarrow[N_2]{115^\circ} [Zn(py)_2(NO_3)_2] + py. \qquad (1)$$
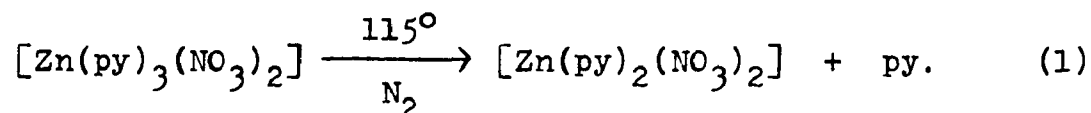
<u>Anal</u>. Calcd for $[Zn(py)_2(NO_3)_2]$: Zn, 18.81; N, 16.11; C, 34.53; H, 2.88. Found: Zn, 18.98; N, 16.26; C, 34.13; H, 2.86.

4. <u>Preparation of Dinitratotris(pyridine)zinc(II) Tripyridine, $[Zn(py)_3(NO_3)_2] \cdot 3py$.</u>

A weighed sample of dinitratotris(pyridine)zinc(II) was finely ground and transferred to a porcelain evaporating dish. The sample was placed in a desiccator over pyridine for nine days at room temperature. During this time the starting material added three moles of pyridine. The sample was then placed in a desiccator at 60 mm pressure and reverted to its original unsolvated weight, thus indicating the reversibility of the solvation process. The original sample and the trisolvate have unique powder patterns. The infrared spectrum of the trisolvate indicates the presence of uncoordinated pyridine. The reaction is given on the following page.

$$[Zn(py)_3(NO_3)_2] + 3py \underset{25°, \ 60 \ mm}{\overset{25°}{\rightleftarrows}} [Zn(py)_3(NO_3)_2] \cdot 3py \quad (2)$$
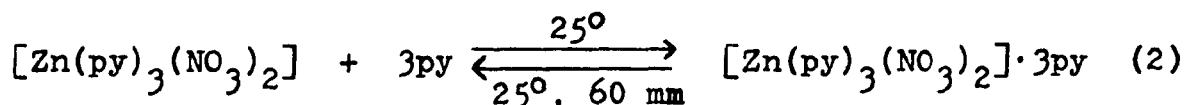
Anal. Calcd for $[Zn(py)_3(NO_3)_2] \cdot 3py$: Zn, 9.85. Found: Zn, 10.29.

5. **Decomposition Products from Dinitratotris(pyridine)-zinc(II)**.

A sample of dinitratotris(pyridine)zinc(II) was gradually heated to temperatures in excess of 250° with frequent weighing. Beyond 130° the sample lost weight very rapidly and the final product was identified as zinc(II) oxide by its powder pattern. No stable intermediate compounds with a lower pyridine content than dinitratobis(pyridine)zinc(II) could be isolated. Whether heated in air or in a dry nitrogen atmosphere, the same product was isolated. The reaction is therefore:

$$[Zn(py)_2(NO_3)_2] \xrightarrow{130°} ZnO + \begin{array}{c} \text{decomposition} \\ \text{products} \end{array} \quad (3)$$
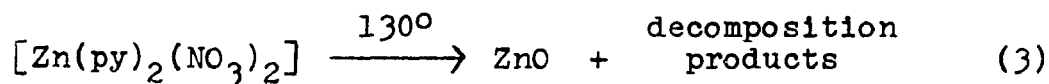
C. **Preparation of Cadmium Complexes**.

The synthesis of some of the cadmium complexes resulted from information obtained from differential thermal analysis (dta) and thermogravimetric analysis (tga) of dinitratotris-(pyridine)cadmium(II). An outline of the dta and tga work is found in subsections F and G.

1. **Preparation of Dinitratotris(pyridine)cadmium(II), $[Cd(py)_3(NO_3)_2]$, from Cadmium Metal**.
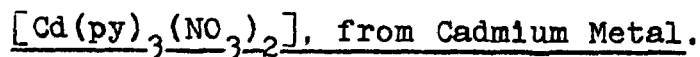
An indirect method of oxidizing cadmium in methanol

was selected for two reasons. The oxidation of cadmium by silver nitrate is very slow, and it was not possible to obtain in methanol a cadmium nitrate solution that was free of silver ion.

Granular bismuth (15 g, 0.072 mole) was added to a magnetically stirred solution of 34 g (0.21 mole) of silver nitrate in 100 ml of dry methanol. The mixture was stirred at room temperature for 30 hr and filtered to remove suspended solids. The filtrate gave a negative Ag^+ test with 6 $\underline{M}$ hydrochloric acid. Cadmium (filings) (12 g, 0.11 mole) was added to the bismuth(III) solution; the mixture was stirred for 30 hr and filtered to remove suspended solids. The filtrate gave a negative bismuth(III) test with stannous chloride. Pyridine (24 ml, 0.31 mole) was added to the cadmium(II) solution, and the mixture was concentrated over an infrared lamp to a final volume of 40 ml. The mixture was placed in a refrigerator at $0°$ for 12 hr to induce crystallization. The white crystalline material was filtered and washed twice with anhydrous ether. The product was recrystallized by dissolving it in a minimal amount of boiling methanol and adding 10 ml of pyridine to the boiling mixture. Precipitation did not occur immediately, but after standing for 14 hr at room temperature large transparent crystals were formed. The product was collected on a sintered-glass filter, and washed successively with two 20-ml portions of methanol and two 20-ml portions of anhydrous ether. The product was finally dried in an evacuated desiccator over silica gel for 4 hr.

<u>Anal</u>. Calcd for $[Cd(py)_3(NO_3)_2]$: Cd, 23.72; N, 14.78;

C, 38.03; H, 3.19. Found: Cd, 24.18; N, 14.84; C, 37.73;
H, 3.10.

2. **Preparation of Dinitratotris(pyridine)cadmium(II),**
    $[Cd(py)_3(NO_3)_2]$, from Cadmium(II) Nitrate Tetra-
    hydrate.

Cadmium(II) nitrate tetrahydrate (30 g, 0.10 mole)
was added to 100 ml of 2,2'-dimethoxypropane in a 250-ml
single-necked, round-bottomed flask fitted with a reflux
condenser. The mixture was refluxed for 22 hr, yielding an
orange-yellow solution. The mixture was filtered to remove
suspended solids, and 24 ml (0.31 mole) of dry pyridine was
added to the warm mixture. The mixture was concentrated over
an infrared lamp to a final volume of 60 ml and cooled to
room temperature, which resulted in the precipitation of a
large quantity of white crystalline material. The reaction
mixture was filtered and the solid washed twice with anhydrous
ether. The product was recrystallized twice using 25-ml por-
tions of pyridine and sufficient methanol to just dissolve
the solid. The product was finally dried for 4 hr in an eva-
cuated desiccator over silica gel.

Anal. Calcd for $[Cd(py)_3(NO_3)_2]$: Cd, 23.72; N, 14.78;
C, 38.03; H, 3.19. Found: Cd, 24.09; N, 14.76; C, 37.77;
H, 3.05.

3. **Preparation of Tetranitratotris(pyridine)dicadmium(II),**
    $[Cd_2(py)_3(NO_3)_4]$, from Dinitratotris(pyridine)cadmium(II).

A weighed sample of dinitratotris(pyridine)cadmium(II)
was finely ground and placed in a porcelain crucible. The

The crucible was placed in a Hoskins combustion furnace, which was heated to 115° and through which a slow stream of dry nitrogen gas was passed. The sample was removed from the furnace, weighed, and reground until no further change in weight was observed. The total time in the furnace was 24 hr. The product was an extremely hygroscopic, white solid which had to be kept under an atmosphere of nitrogen. The total weight change of 24.58% from starting material to final product corresponded to the loss of 1.5 moles of pyridine per mole of the starting material (theoretical weight loss 25.04%). The infrared spectrum and X-ray powder pattern of the final product confirmed that the product was a unique compound. The reaction is therefore:

$$2[Cd(py)_3(NO_3)_2] \xrightarrow[N_2]{115°} [Cd_2(py)_3(NO_3)_4] + 3py. \qquad (4)$$
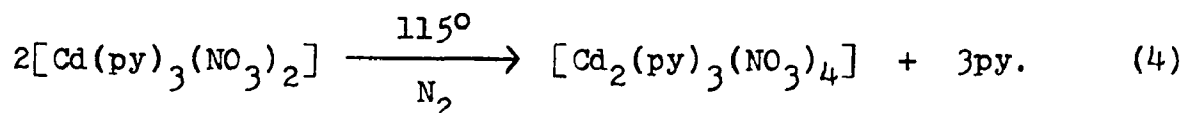
Anal. Calcd for $[Cd_2(py)_3(NO_3)_4]$: Cd, 31.66; N, 13.80. Found: Cd, 31.62; N, 13.85.

4. **Preparation of Dinitratotris(pyridine)cadmium(II) Tri-pyridine, $[Cd(py)_3(NO_3)_2] \cdot 3py$.**

A weighed sample of finely ground dinitratotris(pyridine)cadmium(II) was transferred to a porcelain evaporating dish. The sample was then placed in a desiccator over pyridine for nine days at room temperature. During this time the starting material added three moles of pyridine. The sample was then placed in a desiccator at 60 mm pressure and reverted to its original unsolvated weight, thus indicating the reversibility of the solvation process. The infrared spectrum and

X-ray powder pattern of the product indicated that the trisol-
vate was a unique compound. The reaction is therefore:

$$[Cd(py)_3(NO_3)_2] + 3py \xrightleftharpoons[25^o, 60 \text{ mm}]{25^o} [Cd(py)_3(NO_3)_2] \cdot 3py \quad (5)$$
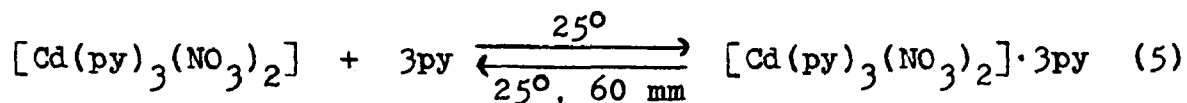
<u>Anal</u>. Calcd for $[Cd(py)_3(NO_3)_2] \cdot 3py$: Cd, 15.81.
Found: Cd, 16.26.

5. <u>Decomposition Products from Dinitratotris(pyridine)-</u>
   <u>cadmium(II)</u>.

A sample of dinitratotris(pyridine)cadmium(II) was
slowly heated to 300° with frequent weighing. Beyond the pla-
teau at 115° the sample gradually lost weight, but no pure
intermediate could be isolated between the tetranitratotris-
(pyridine)dicadmium(II) and the final product, which was
cadmium(II) oxide. The reaction is therefore:

$$[Cd_2(py)_3(NO_3)_4] \xrightarrow{170^o} CdO + \begin{array}{c} \text{decomposition} \\ \text{products} \end{array} \quad (6)$$
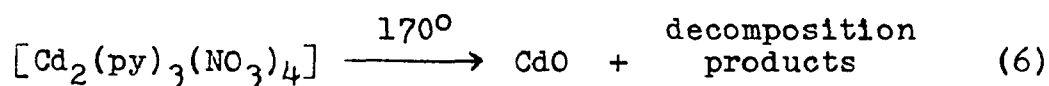
<u>Anal</u>. Calcd for CdO: Cd, 47.56. Found: Cd, 47.11.

D. <u>Preparation of Mercury(II) Complexes</u>.

Some of the synthetic work for the mercury(II) complexes
was suggested by the results of the differential thermal analy-
sis (dta) and thermogravimetric analysis (tga) of dinitrato-
bis(pyridine)mercury(II). An outline of the dta and tga work
is found in subsections F and G.

1. <u>Preparation of Dinitratobis(pyridine)mercury(II)</u>,
   $[Hg(py)_2(NO_3)_2]$, <u>from Mercury(II) Oxide</u>.

Several attempts were made to synthesize the mercury(II)

complexes from mercury(II) nitrate monohydrate, but these efforts were unsuccessful because the monohydrate would not dissolve in suitable solvents. The dinitratobis(pyridine)-mercury(II) was finally prepared using the method of Bullock and Tuck.[31]

Mercury(II) oxide (17 g, 0.080 mole) was added to a mixture of 40 ml of anhydrous ethanol, 80 ml of 10 $\underline{M}$ nitric acid, and 80 ml of dry pyridine in a 250-ml single-necked, round-bottomed flask fitted with a reflux condenser. The mixture was refluxed for one hour, resulting in a pale yellow solution. The warm mixture was filtered to remove suspended solid, then slowly cooled to room temperature. After standing at room temperature for 12 hr, a large quantity of transparent, crystalline material had collected in the bottom of the flask. The reaction mixture was filtered through a sintered-glass filter and the solid was washed successively with two 25-ml portions of methanol and three 25-ml portions of anhydrous ether. The product was recrystallized by dissolving it in a minimal amount of anhydrous methanol to which was then added 10 ml of pyridine. Upon cooling to room temperature and standing for 12 hr, white crystals precipitated from the solution. The product was collected on a sintered-glass filter and was washed as before.

Anal. Calcd for $[Hg(py)_2(NO_3)_2]$: Hg, 41.54; N, 11.61; C, 24.87; H, 2.09. Found: Hg, 41.46; N, 11.56; C, 24.86; H, 2.04.

2. <u>Preparation of Dinitratobis(pyridine)mercury(II)</u>
   <u>Tripyridine, $[Hg(py)_2(NO_3)_2]\cdot 3py$.</u>

A weighed sample of dinitratobis(pyridine)mercury(II)
was finely ground and transferred to a porcelain evaporating
dish. The sample was placed in a desiccator over pyridine
for nine days. During this time the starting material added
three moles of pyridine. The sample was placed in a desic-
cator at 60 mm pressure and reverted to its original unsol-
vated weight, thus indicating the reversibility of the solvation
process. The infrared spectrum and X-ray powder pattern of
the product indicated that the trisolvate was a unique com-
pound. The reaction is therefore:

$$[Hg(py)_2(NO_3)_2] + 3py \underset{25°, \ 60 \ mm}{\overset{25°}{\rightleftarrows}} [Hg(py)_2(NO_3)_2]\cdot 3py \qquad (7)$$
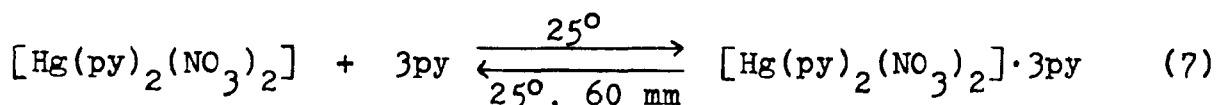
<u>Anal</u>. Calcd for $[Hg(py)_2(NO_3)_2]\cdot 3py$: Hg, 27.86.
Found: Hg, 27.28.

3. <u>Decomposition Products from Dinitratobis(pyridine)-</u>
   <u>mercury(II)</u>.

A sample of dinitratobis(pyridine)mercury(II) was
slowly heated to 256° with frequent weighing. The complex
began to lose weight slowly at 190°, but even after several
hours the total weight loss was very small. At 258° the com-
pound underwent an extremely violent reaction, which resulted
in the complete decomposition of the complex. The final pro-
duct consisted of a mixture of mercury metal and other decom-
position products. During the decomposition at 256°, gases
were evolved which had the odor of nitrogen oxides and pyridine.

Apparently the decomposition is an extremely complex set of redox reactions involving the metal, pyridine, and nitrate groups. The reaction is therefore:

$$[Hg(py)_2(NO_3)_2] \xrightarrow{256^\circ} Hg + \text{decomposition products} \qquad (8)$$
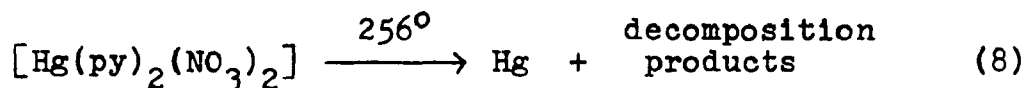
E. Analytical Procedures.

1. Zinc(II) Determination.

Zinc(II) was determined by the method of Welcher.[62] The sample (0.3 to 0.5 g) was dissolved in 40 ml of water, and concentrated ammonia added to the solution until all of the zinc(II) was dissolved. The sample was titrated with 0.5 M disodium ethylenediamine tetraacetate (EDTA) using Eriochrome Black T powder as an indicator, giving a purple to blue end point.

2. Cadmium(II) Determination.

Cadmium was also determined by the method of Welcher,[62] but PAN indicator was used in place of Eriochrome Black T powder. The solution was initially pink, and it was titrated to a yellow end point.

3. Mercury(II) Determination.

Mercury(II) was determined using a modification of the method of Welcher.[62] Because mercury(II) precipitates in basic solution, the sample was dissolved in 40 ml of water followed by the addition of 2 ml of 6 M hydrochloric acid. An excess of EDTA was added to the solution to complex all of the metal, and 10 ml of concentrated ammonia was added to the solution. The excess EDTA was back-titrated with standard zinc(II) sulfate

solution using Eriochrome Black T powder as an indicator. A
blue to purple color change indicated the end point.

4. Pyridine Determination.

An attempt was made to determine pyridine by the
method of Fritz and Hammond.[63] This method involves the po-
tentiometric titration of pyridine in glacial acetic acid
with a standard solution of perchloric acid in glacial acetic
acid. None of the complexes gave a sharp break in the milli-
volt vs volume curves, so the method was abandoned.

5. Carbon, Hydrogen, Nitrogen Determination.

The carbon, hydrogen, nitrogen analyses were performed
by Mr. Ingo Hartmann using the F & M Corp. Model 185 Carbon,
Hydrogen, Nitrogen Analyzer. Other nitrogen analyses were
made with a Coleman Model 29 Nitrogen Analyzer.

F. Differential Thermal Analyses (dta).

The differential thermal analyses were run using a
Fisher Model 360 Linear Temperature Programmer in conjunction
with a Fisher Model 260 Furnace. Both temperature and dif-
ferential temperature were monitored using Texas Instruments'
Servo-riter recorders with one millivolt full-scale deflection.
Various combinations of heating rate and chart speed were tried,
and a heating rate of $10°/min$ with a chart speed of 0.5 in/min
was found to give the best reproducibility. Analyses were
made both under atmospheric conditions and under a stream of
nitrogen; both conditions gave essentially the same curves.
Figure 1 shows the differential thermal analysis for the com-
plex dinitratotris(pyridine)zinc(II), which is representative
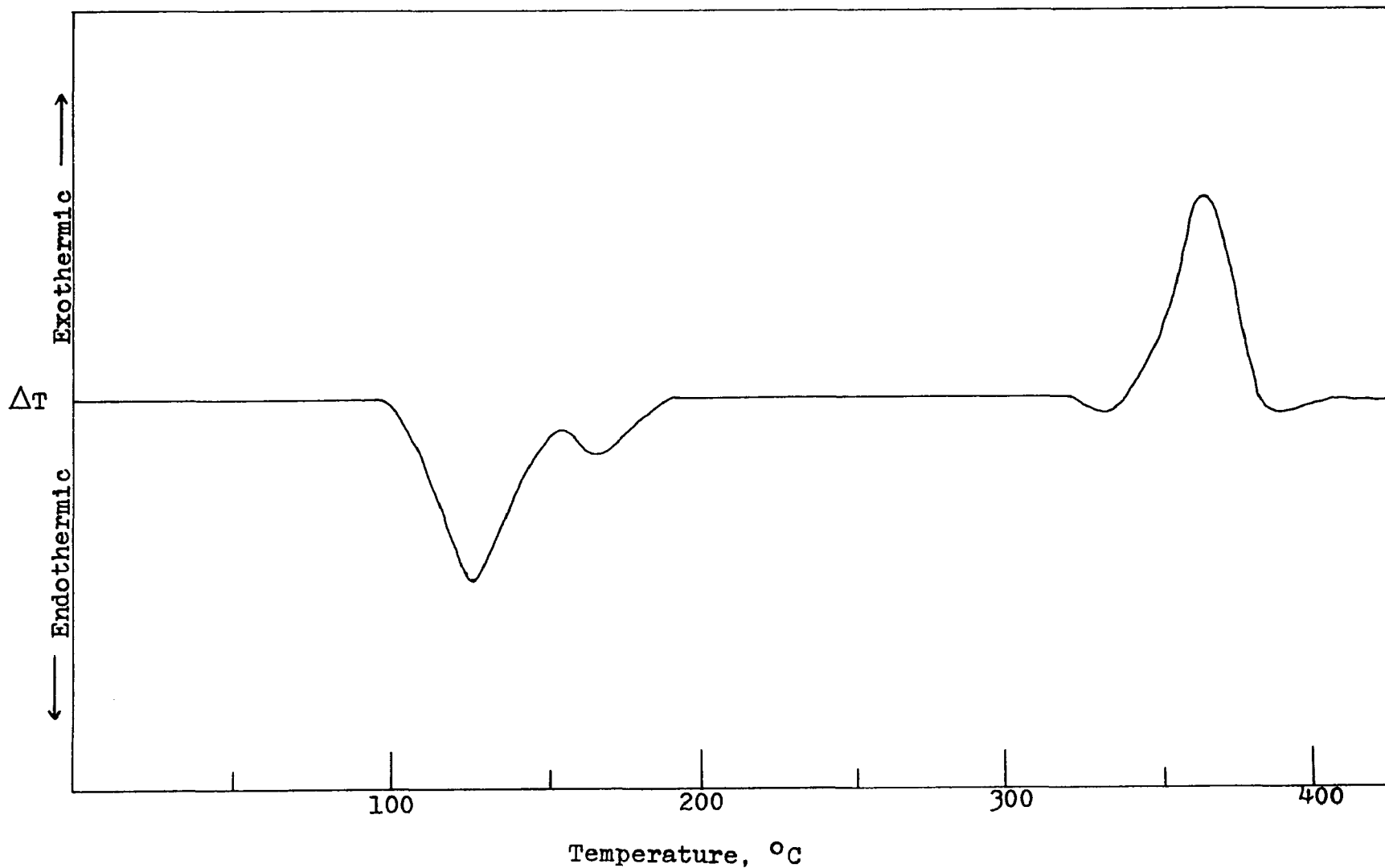
Figure 1. Differential Thermal Analysis Curve of
Dinitratotris(pyridine)zinc(II), $[Zn(py)_3(NO_3)_2]$.

of all the curves. Table I summarizes the data on the dta
runs for all of the complexes studied.

Table I

Differential Thermal Analysis Data for

Pyridine-Nitrate Complexes

Compound	Temperature, $°C$[a],[b]	Peak Characteristics[c]
$[Zn(py)_3(NO_3)_2]$	121	endo; shp; vs
	142	endo; b; w
	342	exo; shp; vs
$[Cd(py)_3(NO_3)_2]$	180	endo; shp; vs
	313	exo; b; vs
$[Hg(py)_2(NO_3)_2]$	179	endo; b; w
	256	exo; shp; vs

[a]temperature taken at maximum of peak. [b]only major peaks are
reported. [c]endo, endothermic; exo, exothermic; shp, sharp;
b, broad; vs, very strong; w, weak.

G. Thermogravimetric Analyses.

The thermal balance used was that constructed by King-
ston,[64] based on a model described by Wendlandt.[65] The tem-
perature was monitored using a Leeds and Northrup Speedomax
recorder with an iron-constantan thermocouple. Temperature
was manually programed using a Powerstat. It was found that
an increase of one Powerstat scale unit per five minutes gave
a relatively linear increase in temperature over the interval

studied. All runs were made under a slow stream of nitrogen.
Sensitivity of the balance appeared relatively constant when
the weight of the sample in the pan was kept between 10 and
65 mg. Figure 2 shows the curves for the complexes studied
by this method. The zinc(II) complex showed a plateau at a
per cent loss in weight of 18.83. This loss in weight cor-
responds to the loss of one mole of pyridine per mole of the
starting material (theoretical weight loss = 18.54%). The
cadmium(II) complex showed a plateau at a per cent weight loss
of 24.58. This loss in weight corresponds to the loss of 1.5
mole of pyridine per mole of the starting material (theoreti-
cal weight loss = 25.04%).

H. Mass Spectral Analyses.

The mass spectra were taken by Miss Ta-Yuen Li on a
Hitachi-Perkin-Elmer Model RMU-6F mass spectrometer. Spectra
were run at a combustion temperature of 130-160° with an ioni-
zation potential of 1500 v. One sample of dinitratobis(pyri-
dine)mercury(II) was also run at a combustion temperature of
230°, and one sample of dinitratotris(pyridine)cadmium(II)
was run at a combustion temperature of 63°. In both cases
the spectra were identical with those reported with combustion
temperatures of 130-160°. The results of the mass spectral
work are summarized in Table II.
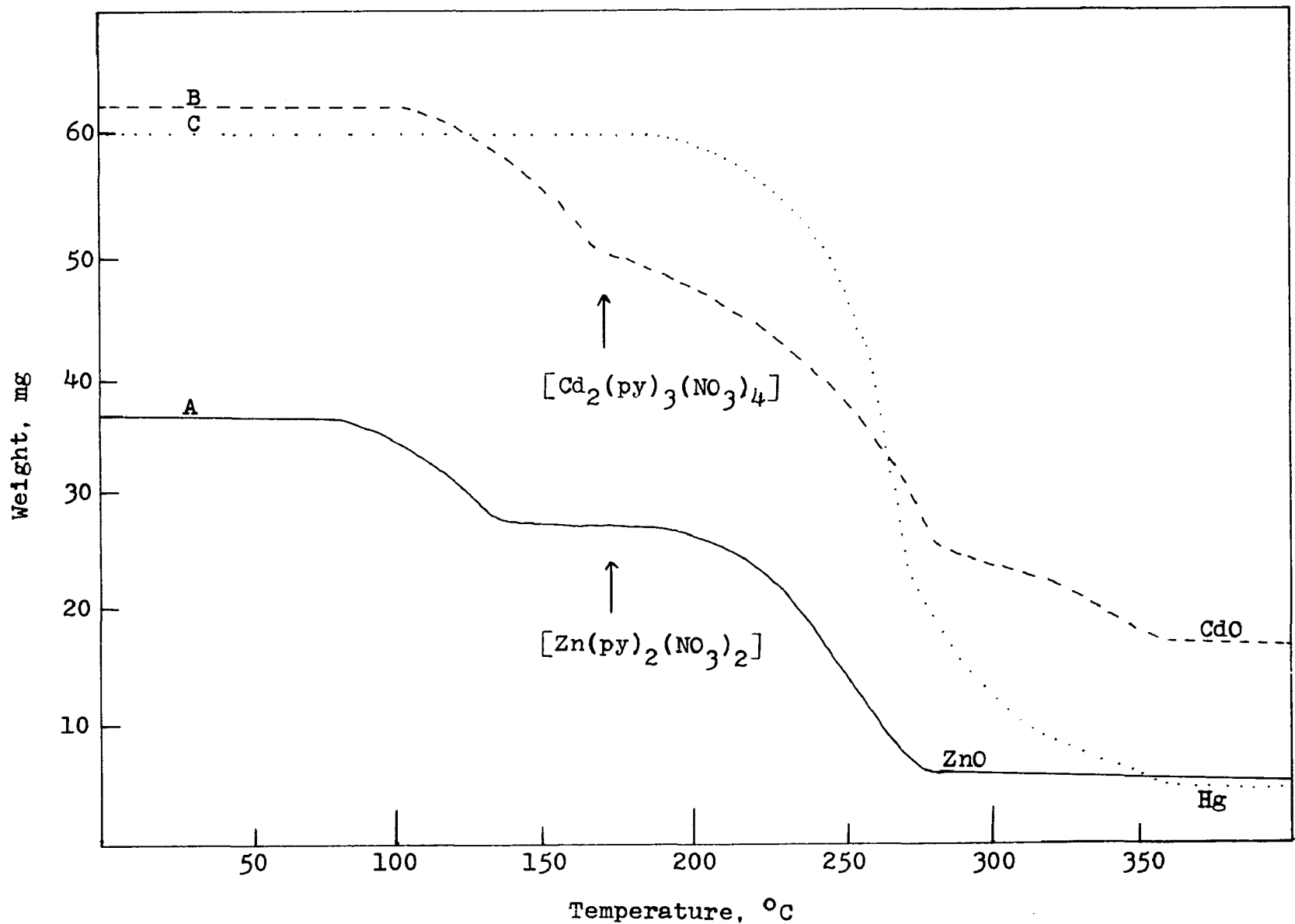
Figure 2. Thermogravimetric Analysis Curves of Metal-Pyridine-Nitrates:

A, $[Zn(py)_3(NO_3)_2]$; B, $[Cd(py)_3(NO_3)_2]$; C, $[Hg(py)_2(NO_3)_2]$.

Table II

Mass Spectral Data for Metal-Pyridine-Nitrates

$$[Zn(py)_3(NO_3)_2]$$

m/e [a]	Relative Abundance [b]	m/e	Relative Abundance
14	4.4	44	2.6
16	2.4	48	2.4
17	5.5	49	7.9
18	15.2	50	34.7
25	2.4	51	50.8
26	21.2	52	92.9
27	8.8	53	12.4
28	67.9	55	2.8
29	2.9	65	2.9
30	2.1	75	2.9
32	21.2	76	2.9
36	1.7	77	2.9
37	5.5	78	14.0
38	6.7	79	100.0
39	16.9	80	6.2
40	2.6	91	17.9
41	3.6	139	0.7
43	2.1	146	4.8

Table II. contd.-

$$[Cd(py)_3(NO_3)_2]$$

m/e	Relative Abundance	m/e	Relative Abundance
13	4.6	49	8.3
14	2.8	50	44.4
15	5.6	51	57.4
16	10.2	52	100.0
17	51.9	53	13.0
25	2.8	55	5.6
26	23.2	56	10.2
27	13.9	57	11.1
28	50.0	65	4.6
29	13.9	74	1.9
31	1.9	75	2.8
32	9.3	76	9.3
36	4.6	77	5.6
37	6.5	78	17.6
38	8.3	79	100.0
39	16.7	80	6.5
40	2.8	93	2.8
41	3.7	104	7.4
42	1.9	105	2.8
43	3.7	149	66.7
44	5.6	150	6.5
48	1.9		

Table II. contd.-

$$[Hg(py)_2(NO_3)_2]$$

m/e	Relative Abundance	m/e	Relative Abundance
25	3.1	52	100.0
26	22.3	53	10.4
27	7.3	55	3.9
28	30.1	56	3.5
29	0.8	57	5.0
30	11.2	69	2.3
31	0.8	71	2.3
32	2.3	74	1.2
36	0.8	75	3.1
37	6.2	76	1.2
38	6.9	77	0.8
39	15.4	78	11.9
40	1.5	79	100.0
41	2.3	80	6.5
42	0.8	148	5.0
43	3.9	198	0.8
44	5.8	199	1.5
48	1.2	200	1.5
49	8.5	201	1.2
50	35.3	202	1.9
51	49.8		

Table II. contd.-

$$[Zn(py)_2(NO_3)_2]$$

m/e	Relative Abundance	m/e	Relative Abundance
12	2.3	48	28.1
13	1.9	49	100.0
14	2.3	50	100.0
15	1.5	51	100.0
16	0.8	52	43.3
17	1.2	53	1.9
24	1.9	54	1.2
25	18.9	55	1.2
26	73.1	56	1.5
27	28.1	61	1.2
28	38.5	62	1.5
29	2.7	63	1.9
35	4.6	73	1.5
36	18.5	74	3.9
37	21.2	75	3.9
38	46.2	78	16.2
39	5.0	79	100.0
40	2.7	81	6.9
42	1.2	84	3.5
43	1.1	86	1.5
47	4.2	100	1.9

Table II. contd.-

m/e	Relative Abundance	m/e	Relative Abundance
102	1.5	134	1.5
103	1.9	140	2.7
104	1.5	146	1.2
130	2.3	147	14.2

[a]ratio of mass to charge. [b]a relative scale based upon a value of 100, assigned to the parent pyridine peak at 79 amu.

I. Magnetic Susceptibility.

The magnetic susceptibilities of the zinc(II), cadmium(II), and mercury(II) complexes were determined by the Gouy Method.[66] The apparatus consisted of a semimicro balance (Mettler H16) mounted above a Varian Model V-4084 Electromagnet. The magnet was powered by a Varian Model 2300A Power Supply and the current was regulated with a Varian Model 2301A Current Regulator. The sample was contained in a double-ended Gouy tube, which was suspended between the poles of the electromagnet (1-in gap) by means of a fine gold chain attached to the balance pan. A magnetic current of 1.8 A was used, which produced a field strength of 8.6 kilogauss. The tube constant was obtained using mercury(II) tetrathiocyanatocobaltate(II) as the standard. The tube constant was calculated using the equation:

$$R = \frac{4820 \cdot S \cdot 10^{-6}}{\Delta W \cdot T}$$

where S is the weight of the sample with the magnet off, ΔW is the difference in weight of the sample with the magnet on and off, and T is the temperature in degrees Kelvin. The tube constant was calculated to be 2.4875×10^{-4} per gram. The mole susceptibilities of the complexes were calculated using the equation:

$$\chi_M = \frac{R \cdot \Delta W \cdot M}{S}$$

where M is the molecular weight. The mole susceptibilities of the complexes were corrected for the diamagnetic contributions of the ligands using the equation:

$$\chi_M' = \chi_M + \chi_M(\text{ligand})$$

The diamagnetic susceptibilities for the ligands were: -18.9×10^{-6} / g-atom for the nitrate group,[66] -49.3×10^{-6}/-g-atom for the pyridine molecule,[67] -15.0×10^{-6} / g-atom for zinc(II), -20.2×10^{-6} / g-atom for cadmium(II), and -40.0×10^{-6} / g-atom for mercury(II).[46,67] The magnetic moments were calculated from the equation:

$$\mu_{eff} = 2.84(\chi_M' T)^{\frac{1}{2}}$$

where μ is the magnetic moment in Bohr Magnetons, χ_M' is the corrected mole susceptibility, and T is the absolute temperature. The results of the magnetic work are summarized in Table III.

Table III

Magnetic Data for the Metal-Pyridine-Nitrate Complexes

Compound	$10^6 \chi'_M$	μ_{eff}, B. M.
$[Zn(py)_3(NO_3)_2]$	-21.6	≈ 0.0
$[Cd(py)_3(NO_3)_2]$	- 4.6	≈ 0.0
$[Hg(py)_2(NO_3)_2]$	- 2.7	≈ 0.0
$[Cd_2(py)_3(NO_3)_4]$	- 5.9	≈ 0.0
$[Zn(py)_2(NO_3)_2]$	18.0	0.21

J. Ultraviolet and Visible Spectra.

Ultraviolet and visible spectra of the zinc(II), cadmium(II), and mercury(II) complexes in the region 6500-2000 Å were run in methanol solution on a Cary 14 Recording Spectrophotometer. The samples were contained in 1-cm silica cells. The spectra were run at a scanning speed of 2.5 Å/sec. Because of the large variation in extinction coefficients between nitrate and pyridine, it was necessary to run the spectra through a series of successive dilutions. All of the compounds have essentially the same spectra, but the extinctions vary from one compound to another. Two peaks were assigned to nitrate absorptions, and the remaining five peaks were assigned to pyridine absorptions. None of the compounds had any absorption in the visible region of the spectrum. A representative spectrum, that of dinitratotris(pyridine)zinc(II),

is shown in Figure 3, and a summary of the spectral data on all of the compounds is given in Table IV.

Table IV

Ultraviolet Absorption Data on the Metal-Pyridine-Nitrates

Compound	λ, mμ	ϵ	log ϵ
$[Zn(py)_3(NO_3)_2]$	199.8	30560	4.485
	239.0	4250	3.628
	245.0	5670	3.754
	250.6	7350	3.867
	256.5	7960	3.901
	262.5	5250	3.720
	298.0	10.9	1.035
$[Cd(py)_3(NO_3)_2]$	200.3	30950	4.491
	238.8	4100	3.613
	245.4	5600	3.748
	250.6	7460	3.873
	256.5	8200	3.914
	261.5	5560	3.745
	296.6	10.6	1.025
$[Hg(py)_2(NO_3)_2]$	200.4	30880	4.490
	239.4	5180	3.714
	245.9	6300	3.799
	250.9	7540	3.877

Table IV. contd.-

Compound	λ, mμ	ε	log ε
	256.5	7885	3.897
	262.5	5200	3.716
	297.5	17.7	1.248
$[Zn(py)_2(NO_3)_2]$	199.5	24000	4.380
	229.0	3120	3.494
	235.0	4060	3.608
	240.0	5000	3.699
	248.0	5500	3.740
	252.0	3200	3.506
	295.0	10.9	1.037
$[Cd_2(py)_3(NO_3)_4]$	201.5	54000	4.732
	228.8	6500	3.813
	232.7	7560	3.878
	239.8	8560	3.931
	245.8	8250	3.916
	250.2	5150	3.712
	297.0	19.8	1.297
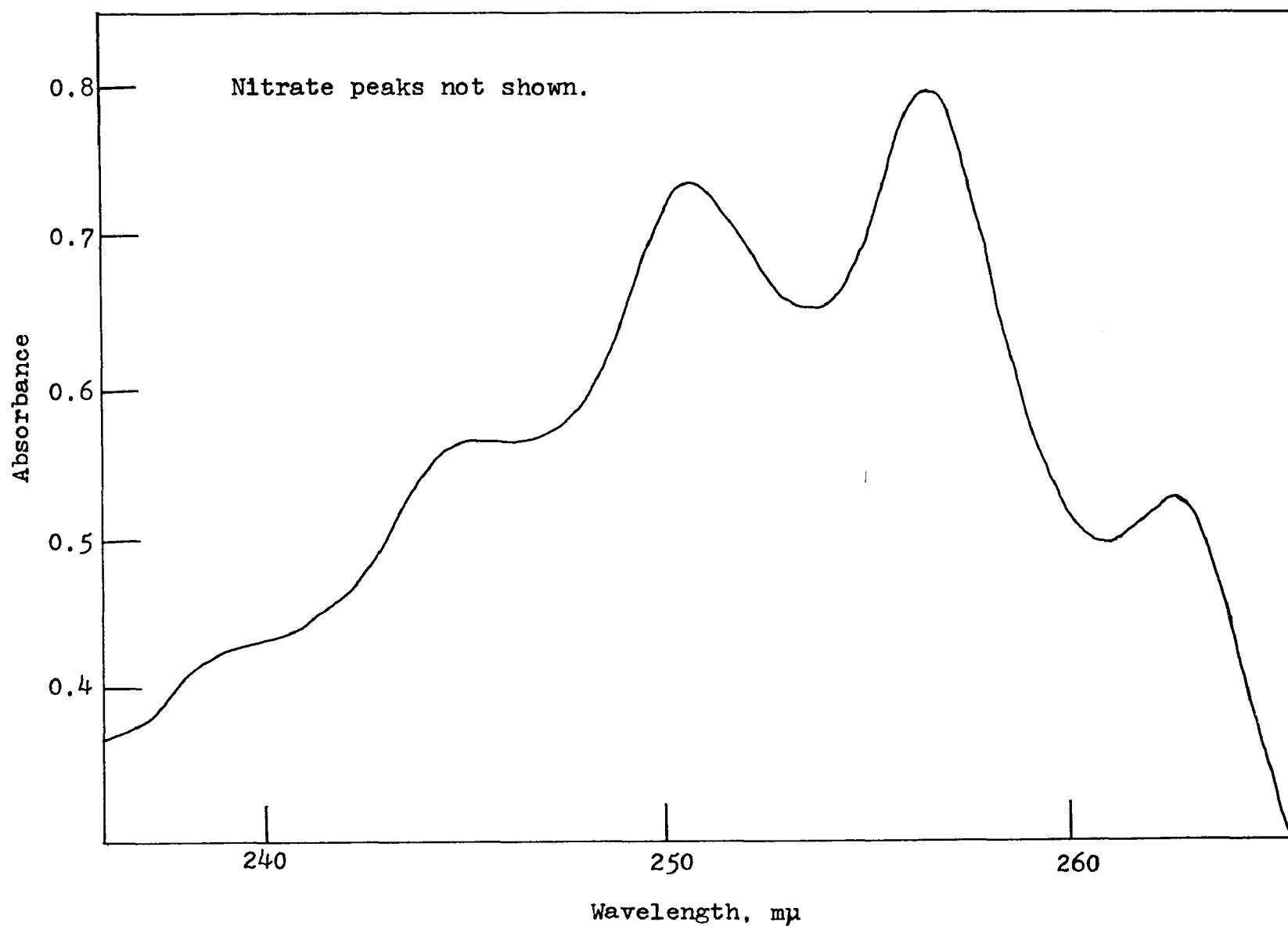
Figure 3. Ultraviolet Spectrum of Dinitrato-
tris(pyridine)zinc(II) in Methanol, (1 x 10^{-4} $\underline{M}$).

K. **Conductivity Measurements**.

The conductivities of the complexes were measured at 25° using a conventional Wheatstone bridge circuit with an oscilloscope to detect the null point. The components of the conductivity apparatus consisted of: audio generator, The Heath Co., Model AG-8; transformer, General Radio Co., 578-A; resistor(R_1), Leeds and Northrup Co.; decade resistor(R_2), Leeds and Northrup Co., 4750; decade resistor(R_3), Heath-Kit, DR-1; and oscilloscope, The Heath Co. The conductivity cell was a specially designed unit for high resistance systems. The conductivity cell was calibrated using 0.02 $\underline{M}$ potassium chloride in aqueous solution. The calculated cell constant was $\theta = 0.04973$ cm^{-1}. Molar conductivities were determined in both dimethylformamide and methanol. Molar conductivities of the 1×10^{-3} $\underline{M}$ solutions are summarized in Table V. Molar conductivities as a function of concentration were also studied in order to ascertain whether the complexes behaved as weak electrolytes in dimethylformamide and methanol. The results of this investigation are shown in Figures 4 and 5.

Table V

Conductivity Data in Dimethylformamide and Methanol[a,b]

Compound	Solvent	Molar Conductance[c]
$[Zn(py)_3(NO_3)_2]$	Dimethylformamide	152
$[Zn(py)_3(NO_3)_2]$	Methanol	164
$[Cd(py)_3(NO_3)_2]$	Dimethylformamide	111
$[Cd(py)_3(NO_3)_2]$	Methanol	123
$[Hg(py)_2(NO_3)_2]$	Dimethylformamide	98
$[Hg(py)_2(NO_3)_2]$	Methanol	156
$[Zn(py)_2(NO_3)_2]$	Methanol	167
$[Cd_2(py)_3(NO_3)_4]$	Methanol	207
1:1 Electrolytes[d]	Dimethylformamide	70-90
1:2 Electrolytes[d]	Dimethylformamide	135-175
1:1 Electrolytes[e]	Methanol	100
1:2 Electrolytes[e]	Methanol	180

[a]all solutions were 1 x 10^{-3} $\underline{M}$. [b]conductivities measured at 25°. [c]in units of $ohm^{-1} cm^2 mol^{-1}$. [d]reference 43. [e]references 68 and 69.
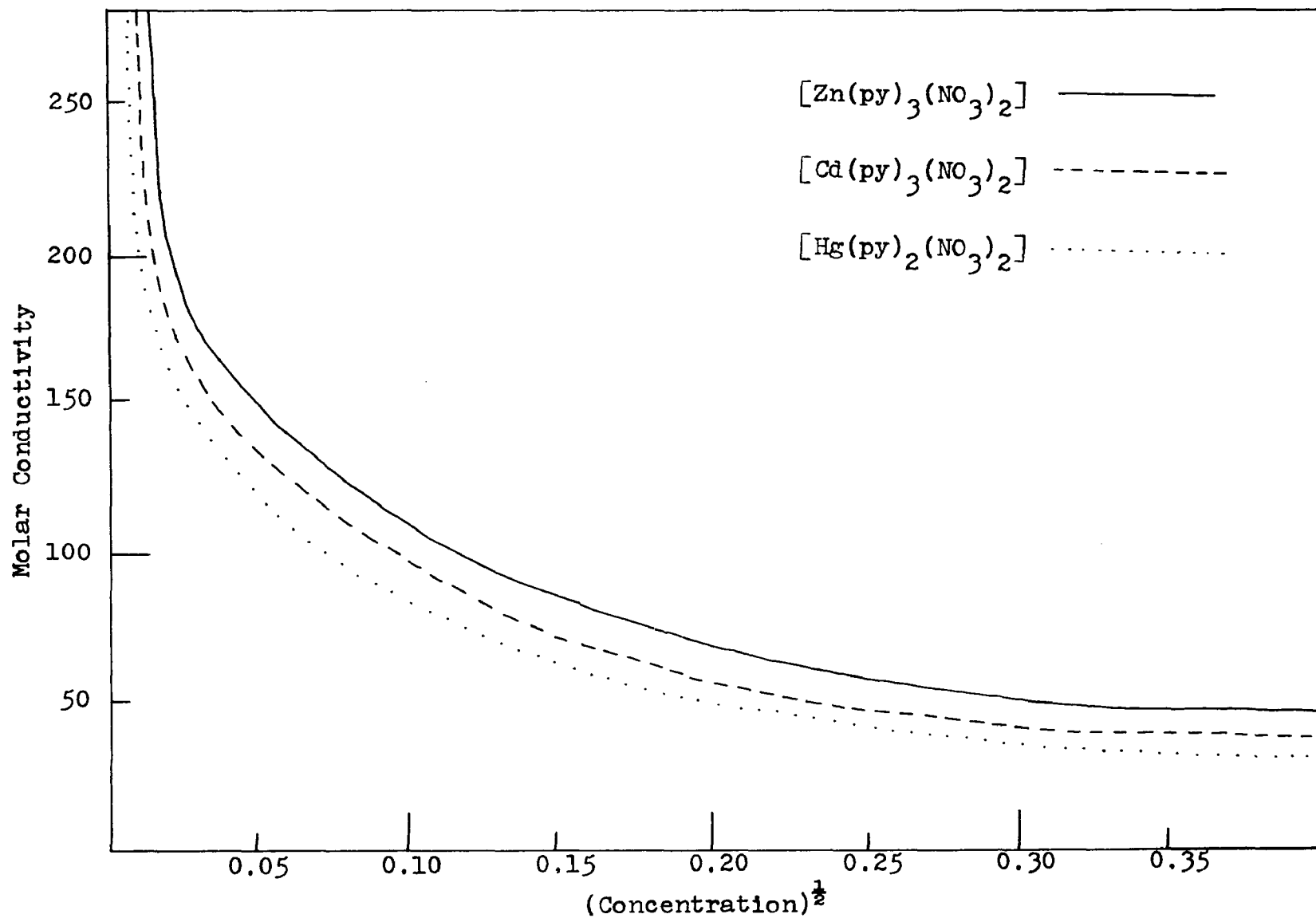
Figure 4. Molar Conductivity vs Square Root of Concentration for the Zinc(II), Cadmium(II), and Mercury(II) Complexes in Methanol.
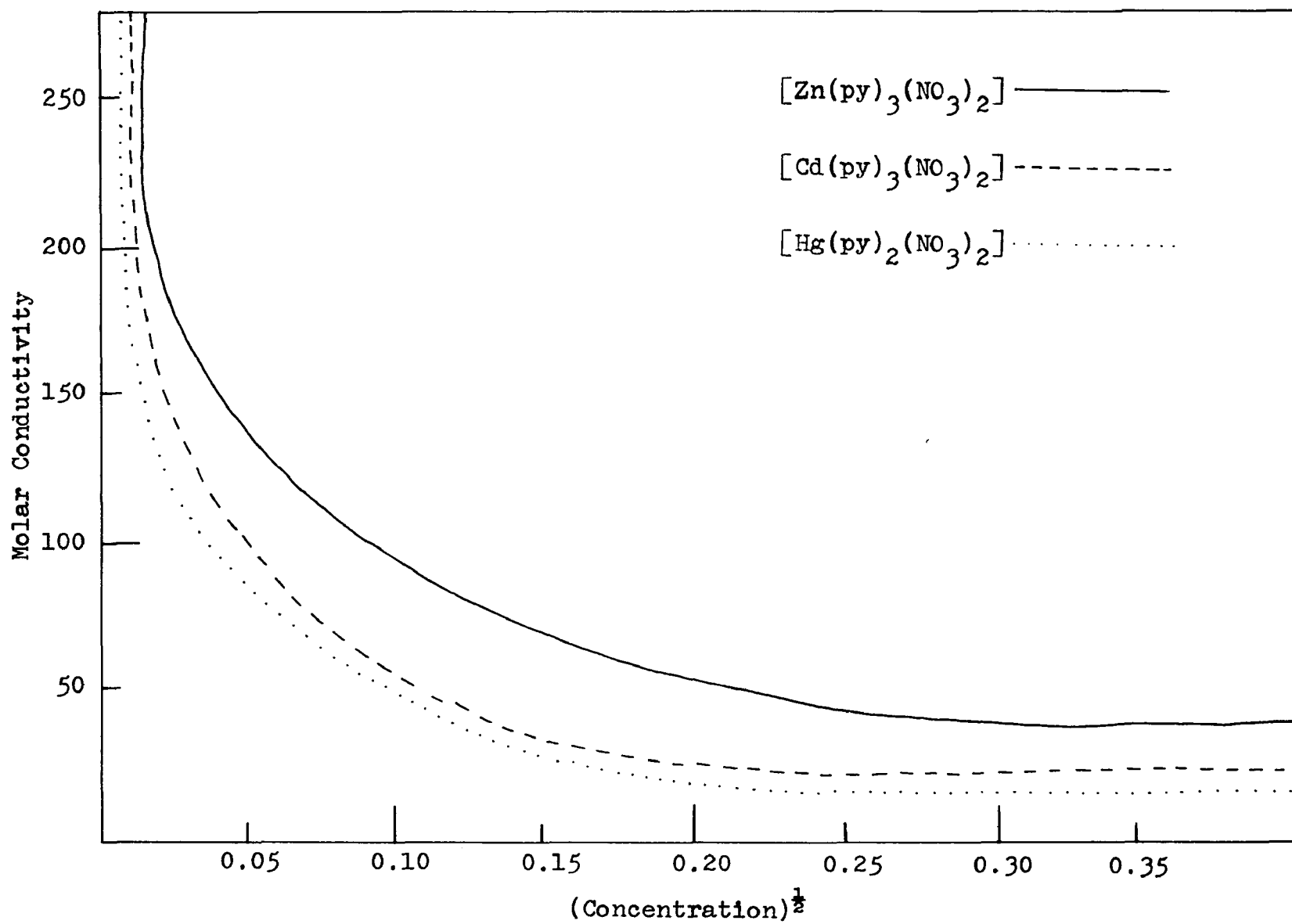
Figure 5. Molar Conductivity vs Square Root of Concentration for the Zinc(II), Cadmium(II), and Mercury(II) Complexes in Dimethylformamide.

L. Molecular Weight Measurements.

Attempts were made to determine the molecular weights of the zinc(II), cadmium(II), and mercury(II) complexes. The instrument used for these determinations was the Mechrolab Model 301-A Vapor-Pressure Osmometer. The determinations were made on 0.1 $\underline{M}$ solutions of the complexes in dimethylformamide. The accuracy of these molecular weights is somewhat questionable due to the instability of the instrument with dimethylformamide. It would have been highly desirable to obtain the molecular weights in some other solvent or by a different method. Unfortunately, all such attempts were unsuccessful because the complexes either decomposed or were not sufficiently soluble in other solvents suitable for such measurements.

Table VI

Molecular Weights of the Zinc(II), Cadmium(II),

and Mercury(II) Complexes in Dimethylformamide.

		Molecular Weight	
Compound	Solvent	Found	Calcd for Monomeric Complexes
$[Zn(py)_3(NO_3)_2]$	Dimethylformamide	478	427
$[Cd(py)_3(NO_3)_2]$	Dimethylformamide	7640	474
$[Hg(py)_2(NO_3)_2]$	Dimethylformamide	129	483

M. X-Ray Powder Diffraction Photographs.

In most cases powder patterns were obtained on finely ground samples mounted in 0.3 mm glass capillaries. The photographs were taken with either a 57.3 or a 115 mm Philips camera using copper ($\lambda = 1.5418$ Å) or iron ($\lambda = 1.9373$ Å) radiation. The powder patterns of the three trisolvates were taken on samples mounted in 0.3 mm capillaries that also contained some free pyridine. The powder patterns for dinitratotris(pyridine)-zinc(II), dinitratotris(pyridine)cadmium(II), dinitratobis-(pyridine)mercury(II), dinitratobis(pyridine)zinc(II), tetra-nitratotris(pyridine)dicadmium(II), and the three trisolvates are reported in Tables VII-XIV. The values for the interplanar spacings (d_{hkl}) were obtained from the $2\theta_{corr}$ values using the X-ray diffraction tables of Fang and Bloss.[70] The relative intensities were estimated visually, and are reported in the following tables as: very very strong (vvs), very strong (vs), strong (s), weak (w), very weak (vw), and very very weak (vvw).

Table VII

X-Ray Powder Diffraction Data for

Dinitratotris(pyridine)zinc(II),

$[Zn(py)_3(NO_3)_2]$

d_{hkl}, Å	Intensity	d_{hkl}, Å	Intensity
8.396	vvw	2.832	vw
7.676	vs	2.789	vw
7.183	vvs	2.731	vw
6.515	vvw	2.682	vw
6.189	vs	2.631	vvw
5.912	vs	2.512	w
5.631	s	2.466	vw
4.844	s	2.434	vw
4.646	s	2.388	vw
4.428	vvs	2.346	vw
4.116	w	2.217	vw
3.965	vvw	2.183	w
3.833	vvs	2.120	w
3.757	w	1.991	vvw
3.656	s	1.926	vvw
3.417	vw	1.780	vvw
3.328	s(b)[a]	1.714	vvw
3.152	w	1.683	vvw
2.972			

[a](b), broad.

Table VIII

X-Ray Powder Diffraction Data for

Dinitratotris(pyridine)cadmium(II),

$$[Cd(py)_3(NO_3)_2]$$

d_{hkl}, Å	Intensity	d_{hkl}, Å	Intensity
8.133	vvw	3.325	vs
7.793	vs	3.024	vvw
7.239	vvs	2.784	vw
6.230	vvs	2.701	vw
5.887	s	2.651	vvw
5.595	s	2.600	vvw
4.911	vw	2.508	vw
4.717	s	2.457	vvw
4.511	s	2.408	vvw
4.149	vw	2.336	vvw
4.045	vvw	2.226	vvw
3.829	vs	2.097	vvw
3.693	w	1.740	vvw
3.612	vw	1.710	vvw
3.449	vvw		

Table IX

X-Ray Powder Diffraction Data for

Dinitratobis(pyridine)mercury(II),

$$[Hg(py)_2(NO_3)_2]$$

d_{hkl}, Å	Intensity	d_{hkl}, Å	Intensity
9.593	vvw	2.805	w
8.690	vvs	2.666	vw
6.328	vs	2.616	vw
6.138	vs	2.558	vw
5.120	vs	2.491	vvw
4.627	s	2.421	w
4.042	s	2.360	w
3.898	s	2.313	vvw
3.763	vw	2.293	vvw
3.621	s	2.223	vw
3.571	s	2.185	vw
3.074	vw	2.140	vw
2.927	vw	2.080	vvw

Table X

X-Ray Powder Diffraction Data for

Dinitratobis(pyridine)zinc(II),

$$[Zn(py)_2(NO_3)_2]$$

d_{hkl}, Å	Intensity	d_{hkl}, Å	Intensity
8.354	s	2.723	w
7.506	vvs	2.672	vw
6.889	vvs	2.516	w
6.194	vvs	2.482	vw
5.754	vvw	2.437	w
4.872	s	2.350	w
4.681	vs	2.304	w
4.437	s	2.183	vw
4.279	w	2.069	vw
3.975	vvs	1.927	vw
3.855	w	1.834	vw
3.734	vs	1.658	vvw
3.566	w	1.536	vvw
3.464	w	1.509	vvw
3.373	w	1.447	vvw
3.222	vw	1.401	vvw
2.887	w	1.323	vvw
2.824	w		

Table XI

X-Ray Powder Diffraction Data for

Tetranitratotris(pyridine)dicadmium(II),

$$[Cd_2(py)_3(NO_3)_4]$$

d_{hkl}, Å	Intensity	d_{hkl}, Å	Intensity
8.522	vvs	2.787	vw
6.588	vvs	2.676	s
6.071	vvw	2.631	vw
5.376	s	2.554	s
5.068	vs	2.378	w
4.611	vs	2.311	vw
4.260	w	2.087	vw
3.857	s	2.021	vw
3.676	s	1.996	vw
3.465	s	1.732	vw
3.230	w	1.673	vvw
3.162	w	1.609	vvw
3.077	w	1.589	vvw
3.016	vw	1.484	vvw
2.878	vw		

Table XII

X-Ray Powder Diffraction Data for

Dinitratotris(pyridine)zinc(II) Tripyridine,

$$[Zn(py)_3(NO_3)_2] \cdot 3py$$

d_{hkl}, Å [a]	Intensity
7.681	vs
7.149	vvs
6.181	vvs
5.934	vs
5.634	s
4.864	s
4.637	s
4.442	vvs
4.107	w
3.834	vvs
3.663	vs
3.414	vvw
3.339	s
3.152	vw
2.963 –	vw
2.787	vw
2.681	vvw
2.503	vw
2.345	vw
2.215	vw
2.184	w
2.118	vw

[a] pattern contains many more very weak lines.

Table XIII

X-Ray Powder Diffraction Data for

Dinitratotris(pyridine)cadmium(II) Tripyridine,

$$[Cd(py)_3(NO_3)_2]\cdot 3py$$

d_{hkl}, Å	Intensity	d_{hkl}, Å	Intensity
7.830	vs	2.781	w
7.225	vvs	2.702	w
6.254	vvs	2.508	w
5.902	s	2.462	w
5.570	s	2.367	w
4.909	vw	2.264	vw
4.690	vs	2.188	w
4.297	vs	2.100	vw
4.139	w	2.020	vw
4.046	vw	1.952	vw
3.813	vs	1.902	vw
3.688	s	1.737	vw
3.607	vw	1.707	vw
3.443	w	1.510	vvw
3.323	vs	1.406	vvw
3.009	w		

Table XIV

X-Ray Powder Diffraction Data for

Dinitratobis(pyridine)mercury(II) Tripyridine

$$[Hg(py)_2(NO_3)_2] \cdot 3py$$

d_{hkl}, Å [a]	Intensity	d_{hkl}, Å	Intensity
8.087 [b]	vvs	2.851	w
7.602 [b]	vvs	2.768	s
6.889	vvs	2.723	s
6.326	vs	2.608	w
5.810	vvw	2.522	w
5.438	vs	2.350	w
5.215	vvs	2.270	s
4.587	vvs	2.194	vw
4.448	vs	2.139	vw
4.208	vw	2.085	vw
4.112	vw	2.040	vw
3.974	w	1.941	vvw
3.767	w	1.793	vw
3.652	w	1.722	vw
3.431	w	1.660	vvw
3.324	vvw	1.620	vvw
3.234	vs	1.568	vvw
3.118	s	1.342	vvw
2.914	s	1.200	vvw

[a] pattern contains many more very weak lines. [b] these lines might not be due to the compound.

N. Infrared Spectra.

The infrared spectra of the solid complexes in the
4000-300 cm^{-1} range were obtained as mulls in Nujol and Halo-
carbon oil in potassium bromide cells. Most spectra were run
using a Beckman IR-12 Recording Spectrophotometer. Survey
spectra on some of the complexes were run using a Perkin-
Elmer Model 337 Grating Infrared Spectrophotometer.

The infrared spectrum of coordinated pyridine can
be readily distinguished from that of uncoordinated pyridine.
The major variations occur in the in-plane bending mode [6(a)]
and in the out-of-plane bending mode [16(b)] of the ring.[72]
Both the in-plane bending mode (602 cm^{-1}) and the out-of-
plane bending mode (404 cm^{-1}) are shifted to higher energy
upon complexation of the pyridine. Table XV lists these two
vibrations for the complexes under investigation. The peaks
indicating uncoordinated pyridine in the trisolvates are also
listed. The remaining pyridine absorption peaks in the com-
plexes are not listed in the table, but they are all consistent
with the assignments of other workers.[50,71-73]

The nitrate absorption peaks for the complexes are
also summarized in Table XV. The nitrate absorptions are
consistent with the presence of coordinated nitrate in the
complexes. The assignments are based upon the reported ab-
sorption spectra for covalent nitrate groups. These assig-
ments have been very well documented by a large number of
workers, and the assignments in Table XV are based upon their
results.[23,52,54,56,74,75]

Table XV

Infrared Absorption Data for the Metal-Pyridine-Nitrates[a]

Compound	(ν_1) NO$_2$ sym. str.	(ν_2) NO str.	(ν_4) NO$_2$ asym. str.	(ν_6) nonplanar def.	6(a)[b] in-plane bend	16(b)[b] out-of-plane bend
$[\text{Zn(py)}_3\text{(NO}_3\text{)}_2]$	1300[c]	1031	1456	818	634	442,428[d]
$[\text{Cd(py)}_3\text{(NO}_3\text{)}_2]$	1280[c]	1030	1468	820	632	420,413[d]
$[\text{Hg(py)}_2\text{(NO}_3\text{)}_2]$	1305[c]	1030	1459	824	658	427,422[d]
$[\text{Zn(py)}_2\text{(NO}_3\text{)}_2]$	1300[c]	1024	1450	813	648,635[d]	428,421
$[\text{Cd}_2\text{(py)}_3\text{(NO}_3\text{)}_4]$	1300[c]	1038	1448	820	638,633[d]	439,434[d]
$[\text{Zn(py)}_3\text{(NO}_3\text{)}_2]\cdot 3\text{py}$	1300[c]	1029	1459	818	634,605[e]	421,403[e]
$[\text{Cd(py)}_3\text{(NO}_3\text{)}_2]\cdot 3\text{py}$	1280[c]	1030	1465	818	632,607[e]	419,412[d] 404[e]
$[\text{Hg(py)}_2\text{(NO}_3\text{)}_2]\cdot 3\text{py}$	1290[c]	1030	1453	819	645,603[e]	420,410[d] 402[e]

[a]sym, symmetric; asym, asymmetric; str, stretch; def, deformation; all absorptions in cm^{-1}. [b]pyridine peaks. [c]broad. [d]doublet. [e]peaks from uncoordinated pyridine.

O. <u>Far-Infrared Spectra</u>.

The far-infrared spectra of the solid complexes in the 400-33 cm^{-1} range were obtained as mulls in Nujol between high density polyethylene plates. The spectra were recorded using a Beckman IR-11 Recording Spectrophotometer at a dispersion of 20 cm^{-1}/in. Table XVI summarizes the results obtained. Figures 6 and 7 are approximate reproductions of the curves obtained in the far-infrared region of the spectrum.

Table XVI

Far-Infrared Absorption Bands for the Metal-Pyridine-Nitrates

Compound	ν M-O[1]	ν M-N	Other Bands
$[Zn(py)_3(NO_3)_2]$	210 (s,b)[2]	200 (s,b)	150 (w)
$[Cd(py)_3(NO_3)_2]$	190 (s)[3]	160 (s,b)	100 (w) 72 (w,b)
$[Hg(py)_2(NO_3)_2]$	303 (w) 248 (w)	220 (w)[4] 165 (m)	130 (s,b) 110 (s,b)
$[Zn(py)_2(NO_3)_2]$	305 (s,shp) 285 (s,shp)	250 (w,b) 210 (s,b)	160 (m,b) 90-130 (m,b)
$[Cd_2(py)_3(NO_3)_4]$	250 (m)	205 (s,b)	160 (s,b) 90 (m,b)

[1] all absorptions reported in cm^{-1}. [2] w, weak; m, medium; s, strong; b, broad.
[3] broad band between 210 and 200 which is split into doublet. [4] peaks at 160 and 190 are a broad doublet.
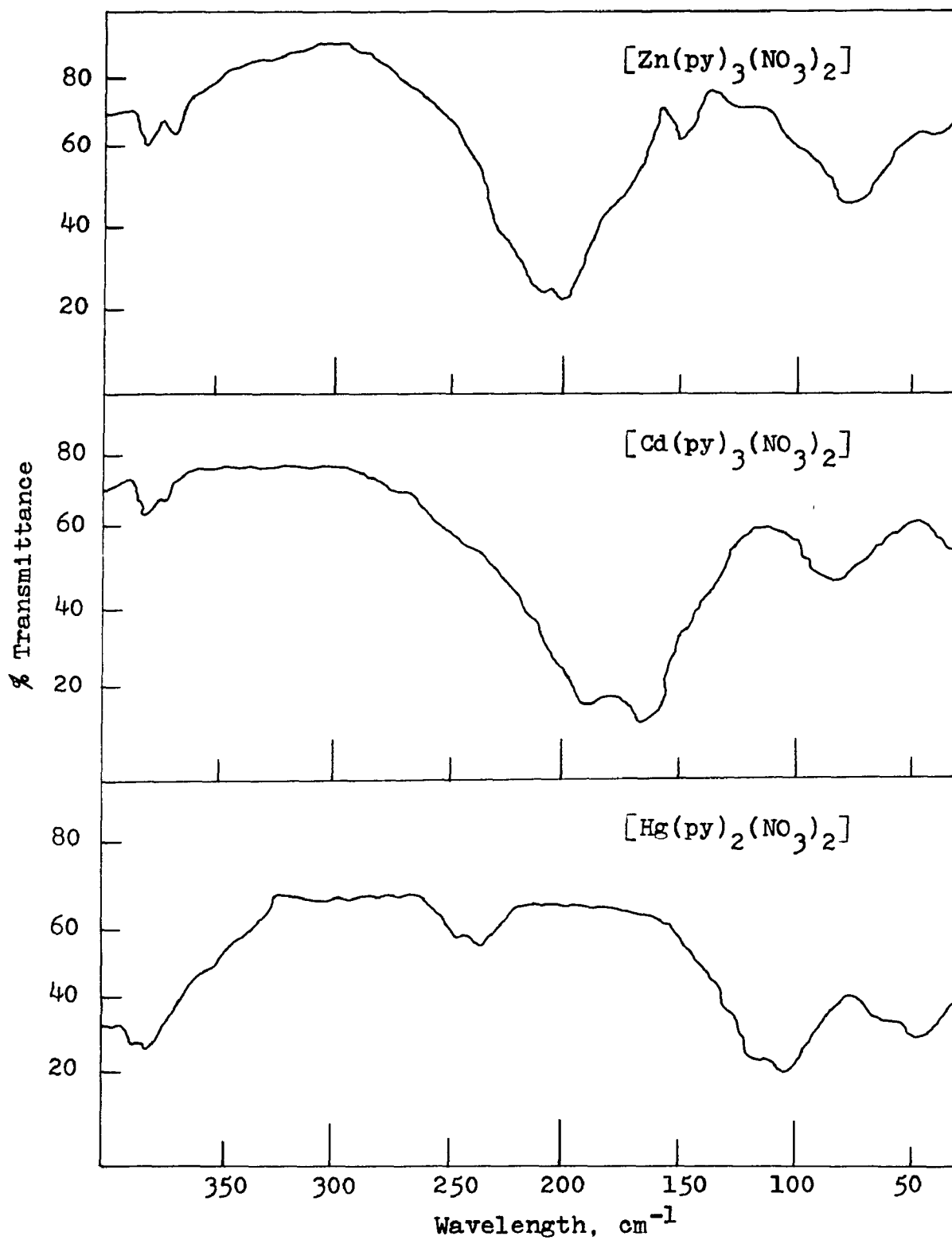
Figure 6. Infrared Spectra of Dinitratotris(pyridine)-
zinc(II), Dinitratotris(pyridine)cadmium(II), and Di-
nitratobis(pyridine)mercury(II).
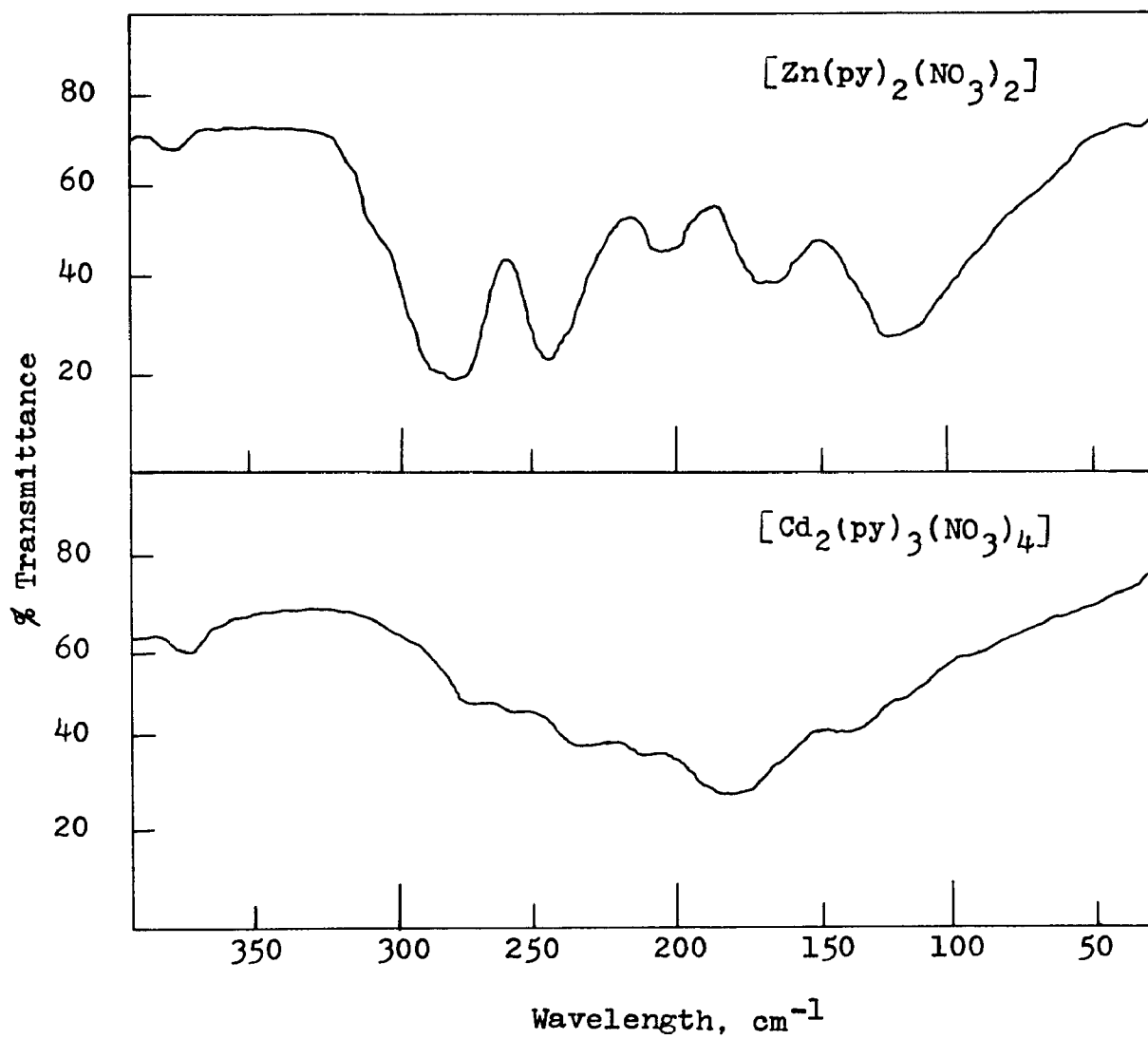
Figure 7. Infrared Spectra of Dinitratobis(pyridine)-zinc(II) and Tetranitratotris(pyridine)dicadmium(II).

III. RESULTS AND DISCUSSION

A. Pyridine Complexes Found in this Work.

1. Zinc(II) Nitrate Complexes.

The zinc(II) nitrate complexes which have been prepared in this work include:

$[Zn(py)_3(NO_3)_2]$, dinitratotris(pyridine)zinc(II);

$[Zn(py)_2(NO_3)_2]$, dinitratobis(pyridine)zinc(II);

$[Zn(py)_3(NO_3)_2] \cdot 3py$, dinitratotris(pyridine)zinc(II) tripyridine.
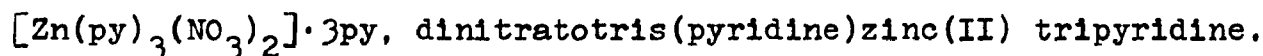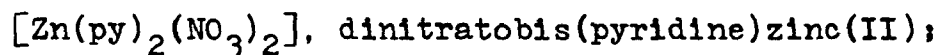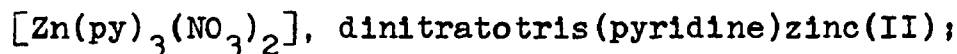
The three complexes are interrelated through the addition or loss of pyridine. Reactions (1), (2), and (3), (cf. pp 6,7) support the following reaction scheme:

$$[Zn(py)_3(NO_3)_2] \cdot 3py \;\underset{25^{\circ},\ 60\ mm}{\overset{25^{\circ},\ py}{\rightleftharpoons}}\; [Zn(py)_3(NO_3)_2]$$

$$115^{\circ} \Big\downarrow N_2$$

$$\text{decomposition products} \quad ZnO \;\xleftarrow{>130^{\circ}}\; [Zn(py)_2(NO_3)_2]$$
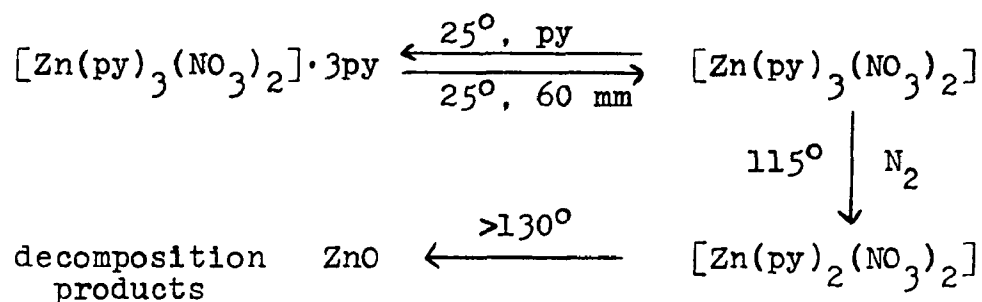
Although the literature contains numerous reports of zinc(II) complexes with a wide variety of anions and organic ligands, very little work has been reported on zinc(II) nitrate complexes. Zinc(II) nitrate complexes with aniline and substituted anilines,[20], trimethyl- and triphenylphosphine oxide, triphenylarsine oxide,[21,22] 2-picoline, quinoline, isoquinoline,[23] acetonitrile,[24] o-phenanthroline,[25] substituted pyridines,[26] picolinic amides,[27] and dimethyl sulfoxide[28] have been reported. Aside from the above complexes, the only other zinc(II) nitrate complexes found in the literature were

$Zn(py)_2(NO_3)_2 \cdot 2H_2O$ reported by Grossman[32] and dinitratotris-(pyridine)zinc(II) reported by Frank and Rogers.[11]

In this work dinitratotris(pyridine)zinc(II) was prepared by two different methods. The products from both syntheses had identical powder patterns and elemental analyses. The compound was very stable at room temperature and did not appear to be hygroscopic. It should be noted, however, that when this complex was crystallized from either methanol or chloroform, the crystals in solution were transparent. When the complex was filtered and dried, the crystals became cloudy. No explanation for this change is apparent, but X-ray powder patterns and elemental analyses of both the transparent and cloudy crystals were identical.

Biagetti[3,4] has shown that certain copper(II), nickel(II), and cobalt(II) pyridine-nitrate complexes, which contain crystal pyridine, can be prepared. A similar situation was found to occur with dinitratotris(pyridine)zinc(II). When this complex was placed in an atmosphere of pyridine at 25°, the compound added three moles of pyridine. The new complex was not an exceptionally stable species, since it readily lost the three moles of pyridine at room temperature and at a pressure of 60 mm. The fact that this was indeed a unique compound was strongly inferred by the observation that the dinitratotris(pyridine)zinc(II) consistently picked up exactly three moles of pyridine. An exact stoichiometric relationship is generally a good indication that adsorption, which was the other possible explanation for the addition of three moles of pyridine, does not occur. Furthermore, the X-ray

powder photographs of the trisolvate and the parent compound were sufficiently unique to indicate that the two compounds were different. The infrared also indicated that the hexapyridine complex contained both coordinated and uncoordinated base.

Dinitratobis(pyridine)zinc(II) was prepared by the thermal decomposition of dinitratotris(pyridine)zinc(II) at 115° in a nitrogen atmosphere. The fact that this compound should exist was indicated by both the dta and tga of the tris(pyridine) complex. It should be mentioned that the decomposition temperature was rather crucial for this particular complex, because at a temperature of 130° the complex began decomposing to zinc(II) oxide. The integrity of this complex was established using a variety of techniques, which will be discussed later in the thesis. The bis(pyridine) complex was rather unique for a zinc(II) complex in that it was pale pink. The first inclination was to ascribe the color to some trace contamination. This explanation, however, was not acceptable in view of the fact that several different samples of dinitratobis(pyridine)zinc(II) prepared from both zinc(II) nitrate hexahydrate and zinc metal were used to synthesize the bis-(pyridine) complex, and each time the same pale pink complex was obtained. Visible and ultraviolet spectra of the complex were of no help in clarifying the situation.

The decomposition of dinitratobis(pyridine)zinc(II) was found to occur very rapidly with no stable intermediate compounds formed. The decomposition was no doubt a complex set of redox reactions involving all three components of the

complex. The only product identified from the decomposition was zinc(II) oxide, which was identified by its X-ray powder pattern.

2. Cadmium(II) Nitrate Complexes.

The cadmium(II) nitrate complexes which have been synthesized in this work include:

$[Cd(py)_3(NO_3)_2]$, dinitratotris(pyridine)cadmium(II);

$[Cd_2(py)_3(NO_3)_4]$, tetranitratotris(pyridine)dicadmium(II);

$[Cd_2(py)_3(NO_3)_2] \cdot 3py$, dinitratotris(pyridine)cadmium(II) tripyridine.

The three complexes are interrelated through the addition or loss of pyridine. Reactions (4), (5), and (6) (cf. pp 10,11) give the following reaction scheme:

$$[Cd(py)_3(NO_3)_2] \cdot 3py \underset{25^\circ, \ 60 \ mm}{\overset{25^\circ, \ py}{\rightleftharpoons}} [Cd(py)_3(NO_3)_2]$$

$$115^\circ \downarrow$$

$$\text{decomposition products} + CdO \xleftarrow{\ >170^\circ\ } [Cd_2(py)_3(NO_3)_4]$$
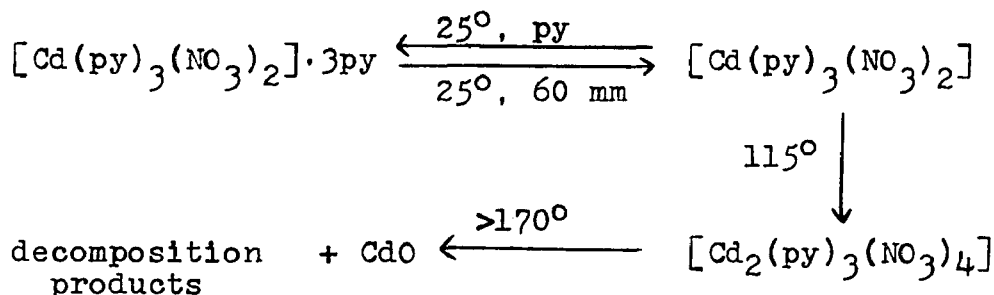
As in the case of zinc(II) nitrate, the number of organic cadmium(II) nitrate complexes which have been reported in the literature is very small. The various complexes which have been reported include those with the ligands aniline and substituted anilines,[20] thiourea,[37] o-phenanthroline,[30] acetonitrile,[24,29] and the complex $Cd(py)_2(NO_3)_2 \cdot 2H_2O$[32] No anhydrous pyridine complex of cadmium(II) nitrate was found in the literature.

Dinitratotris(pyridine)cadmium(II) was prepared by

two independent routes. The products obtained by both methods had identical powder patterns and the same elemental analyses. The tris(pyridine) complex was very stable at room temperature and did not appear to be hygroscopic. The complex was soluble in water and most polar organic solvents, but was insoluble in weakly polar and nonpolar solvents. In most cases, however, the solutions of the complex had a strong odor of pyridine, which indicated that solvolysis had taken place. The tris(pyridine) cadmium[11] complex was similar to its zinc(II) analogue in that the transparent crystals obtained by crystallization from either methanol or chloroform became cloudy upon removal from solution.

When dinitratotris(pyridine)cadmium(II) was placed in a pyridine atmosphere, the complex added three moles of pyridine. As in the case of the zinc(II) complex, the gain and loss of the pyridine was found to occur reversibly, and always with the same stoichiometry of three moles of pyridine to one mole of the parent compound. The X-ray powder patterns of the tris and hexakispyridine complexes were sufficiently different to indicate that the hexakispyridine complex was in fact a unique compound, as opposed to being simply the parent compound with three moles of adsorbed pyridine. The infrared also indicated that the hexakispyridine complex contained both coordinated and uncoordinated base.

Tetranitratotris(pyridine)dicadmium(II) was prepared by the thermal decomposition of dinitratotris(pyridine)cadmium(II) at 115° in a slow stream of dry nitrogen. The stoichiometry of this complex was rather unusual, but not completely

surprising. Other workers have found similar stoichiometries for cadmium(II) complexes.[7,28] The compound was very hygroscopic, so any manipulations with the solid were done in a nitrogen atmosphere. The far-infrared, dta, tga, and X-ray powder pattern all confirmed the existence of this complex as a unique compound.

3. Mercury(II) Nitrate Complexes.

Two pyridine complexes of mercury(II) were found in this investigation. They are dinitratobis(pyridine)mercury(II), $[Hg(py)_2(NO_3)_2]$, and dinitratobis(pyridine)mercury(II) tripyridine, $[Hg(py)_2(NO_3)_2] \cdot 3py$. As in the cases of the zinc(II) and cadmium(II) complexes, the tripyridine compound was obtained by the reaction of the bis(pyridine) compound in an atmosphere of pyridine. A combination of reactions (7) and (8) (cf. pp 13,14) led to the following reaction scheme:

$$[Hg(py)_2(NO_3)_2] \cdot 3py \underset{25°, \ 60 \ mm}{\overset{25°, \ py}{\rightleftharpoons}} [Hg(py)_2(NO_3)_2]$$

$$256° \downarrow$$

$$Hg + \text{decomposition products}$$
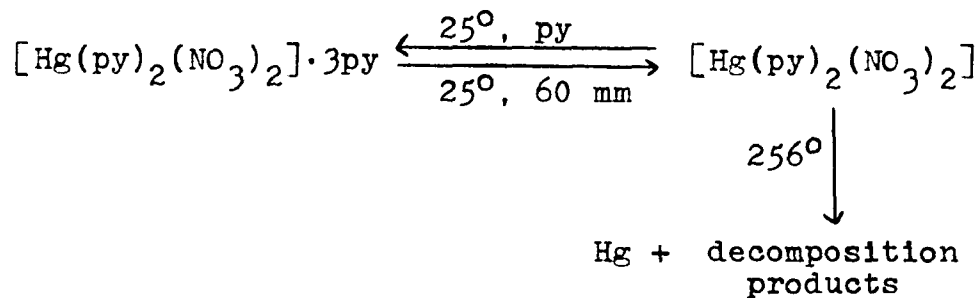
Although the coordination chemistry of mercury(II) complexes has been extensively studied, practically nothing is known about mercury(II) nitrate complexes with organic ligands. Reports of only two such complexes were found in the literature. The first of these was prepared by Grossman[32] and has the formula $Hg(py)_2(NO_3)_2 \cdot 2H_2O$, but he did essentially nothing with the compound. The second was the same

bis(pyridine) complex prepared in this work, and in this case[31] only the infrared spectrum of the compound was given.

Dinitratobis(pyridine)mercury(II) was an extremely stable species in the solid state. Even up to a temperature of 180° the compound remained essentially intact. It was markedly less soluble than its zinc(II) and cadmium(II) counterparts in both water and polar organic solvents, and was virtually insoluble in nonpolar solvents. It has been well established that mercury(II) forms exceptionally strong covalent bonds,[28] which accounts for the differences in thermal stability and solubility between the mercury(II) complex and the zinc(II) and cadmium(II) complexes.

Similar to the zinc(II) and cadmium(II) complexes, dinitratobis(pyridine)mercury(II) reversibly and stoichiometrically added and liberated three moles of pyridine at room temperature. The X-ray powder pattern for the trisolvate was once again quite different from its parent compound, which indicated that the trisolvate was a unique compound and not simply the parent compound with adsorbed pyridine.

Consistent with Bullock's report,[31] dinitratobis(pyridine)mercury(II) decomposed explosively at 256°. The final products from this reaction consisted of mercury metal plus other decomposition products. The fact that mercury(II) was reduced to mercury metal immediately suggested the interaction of pyridine in the redox system, for it is highly unlikely that the nitrate group would function as a reducing agent.

B. **Differential Thermal and Thermogravimetric Analyses.**

Because dta and tga were used in conjunction with one another, they will be discussed together. The differential thermal analysis data are summarized in Figure 1 (p 16) and Table I (p 17). The thermogravimetric analysis data are shown in Figure 2 (p 19). These two techniques are extremely useful tools which, when used in conjunction with one another, can provide a great deal of information concerning the pathway by which a thermal decomposition occurs. Beech and Mortimer[2] have reported a whole series of such investigations on transition metal halide complexes, and Wendlandt[15] has studied an extensive series of complexes of the formulas $M(py)_4X_2$ and $M(py)_2X_2$, where the divalent metals M included Co, Ni, Cd, Cu, Zn, Mn, and X was SCN^-, I^-, Br^-, Cl^-, or $\frac{1}{2} C_2O_4^=$. However, little work has been reported on the decomposition of metal-nitrate complexes.

The dta of dinitratotris(pyridine)zinc(II) showed two endothermic peaks, at 121° and 142°, and one exothermic peak at 342°. The tga of the same complex showed two well-defined breaks in the curve. The first of these occurred at about 120° and corresponded to a weight loss of one mole of pyridine per mole of the starting material. Therefore, the first peak in both the dta and tga corresponded to the formation of dinitratobis(pyridine)zinc(II). The second peak in the dta corresponded to the slow loss of the second two moles of pyridine. This, once again, was consistent with the tga, which showed that no stable intermediate complex was formed after the bis(pyridine) complex and before the

final decomposition products. The third break in the dta indicated the formation of the metal oxide, which also agreed with the results from the tga. The peak at 142°, which had no counterpart in the tga, was probably due to either a crystal modification or volatilization of the freed pyridine.

The tga of dinitratotris(pyridine)cadmium(II) indicated that perhaps two stable intermediates should be present. It was found, however, that at temperatures in excess of 170° decomposition leading to cadmium oxide occurred. The break in the tga curve at 160° corresponds to a per cent weight loss of 24.58, and indicates the liberation of 1.5 moles of pyridine per mole of the starting material (theoretical weight loss = 25.04%). This weight change agrees with the formation of tetranitratotris(pyridine)dicadmium(II). Because cadmium(II) oxide is formed at temperatures in excess of 170°, the second deflection in the tga curve is not indicative of any pure isolatable compound. The dta and tga curves of dinitratotris(pyridine)cadmium(II) are qualitatively in agreement with one another. The endothermic and exothermic peaks are assigned to the liberation and volatilization of pyridine and the formation of cadmium(II) oxide, respectively.

Dinitratobis(pyridine)mercury(II) showed two peaks in the dta. There was an endothermic peak at 179° and an exothermic peak at 256°. The endothermic peak at 179° was in agreement with the tga curve, which indicated the initial loss of pyridine at this temperature. The very strongly exothermic peak at 256° in the dta corresponded to an

exceedingly rapid decomposition reaction, which resulted in the formation of mercury metal and other decomposition products. This was in agreement with the tga, which indicated that almost the entire sample was volatilized at $256°$. The slope of the tga curve between the first indication of a weight loss and the final product was very steep, which indicated that the decomposition was quite rapid. The fact that there were no plateaus in the tga indicated that no stable intermediate compounds were present. This also was in agreement with the failure to isolate either the monopyridine complex or anhydrous mercury(II) nitrate.

C. Mass Spectral Analyses.

The data on the mass spectra of the complexes are summarized in Table II (p 20). It was initially hoped that the mass spectra might either provide insight into the mechanism by which thermal decomposition occurs or provide an extremely accurate way of determining the molecular weights of the complexes.

The mass spectra for all of the complexes showed the characteristic fragmentation pattern for pyridine. The large sets of peaks centered around 79 amu and 55 amu are characteristic of pyridine. The peak at 55 amu corresponds to the loss of HCN from the pyridine molecule.[38] All of the spectra had a peak which could be assigned to the metal in the 2+ oxidation state. Peaks assignable to the molecular ions were absent in every case. Drastic changes in both the combustion temperature and ionization potential seemed to have no noticeable effect on the spectra.

Other peaks which were somewhat diagnostic of the means by which decomposition occurred were assignable to NO^+, N_2O^+, N_2^+, and CO^+ (either or both of the latter two). The mass spectra proved to be only moderately useful in determining decomposition pathways. The data indicated that complete decomposition of the molecules occurred in the electron beam, and that the reactions involved reduction of the nitrate groups.

It was interesting to note that no peaks could be found that corresponded to the metal oxides. This meant that one of two things occurred. Either the metal oxides were not formed or any metal oxides formed in the combustion chamber were not sufficiently volatile to reach the ionization chamber.

D. <u>Magnetic Susceptibility Measurements on the Complexes.</u>

The magnetic moments of the complexes were measured in order to ensure that all of the complexes contained metal ions in the 2+ state; <u>i.e.</u>, outer electronic configurations of d^{10}.

Data on the magnetic moments of the zinc(II), cadmium(II), and mercury(II) complexes are summarized in Table III (p 26).

Within experimental error, the magnetic moments were all zero, indicative of the expected diamagnetic d^{10} system.

E. <u>Ultraviolet and Visible Spectra.</u>

Because all of the complexes studied in this work were diamagnetic, d^{10} species, the visible region of the

spectrum was expected to be nondescript. This expectation
was substantiated by the spectra of the compounds. Figure
3 (p 29) and Table IV (p 27) summarize the data on the ultra-
violet spectra of the complexes.

The pyridine absorption bands in both the free and
the complexed state have been discussed rather extensive-
ly.[39-42] Jørgensen[40] has said that the internal pyridine
transition has a vibrational structure consisting of five
components. When pyridine becomes complexed, some of the
vibrational fine structure is sometimes lost due to signi-
ficant changes in the π electron system of pyridine, but
frequently the five bands remain essentially unchanged.

In each of the complexes the five bands located at
approximately 239, 246, 251, 256, and 262 mμ were therefore
assigned to the vibrationally excited internal electronic
transitions of pyridine. Changes in λ_{max} and ϵ were not
sufficiently large to be significant.

The two other bands in each of the complexes were
assigned to nitrate absorptions. Addison and Sutton[28] have
discussed the nitrate group transitions and assigned the weak
band at 302 mμ (ϵ = 7.2) to a $\pi^* \leftarrow$ n transition, and the in-
tense band at 200 mμ (ϵ = 10^4) to a $\pi^* \leftarrow \pi$ transition. For
the zinc(II), cadmium(II), and mercury(II) complexes, the
bands which were located in approximately these positions
were therefore assigned to these two nitrate transitions.
Again there could be no significance attached to the slight
variations in λ_{max} or in the value of the molar extinction
coefficients.

F. Conductance Measurements.

Conductance measurements were made on the complexes, and a summary of these data is found in Figures 4 and 5 (pp 32, 33) and in Table V (p 31). Because of the limited solubility of the complexes, relatively polar solvents had to be used for these measurements. It would have been more desirable to use a noncoordinating solvent, but the solubility requirements made this impossible.

Because the infrared indicated that the nitrate groups were coordinated in these complexes, it was expected that the complexes would behave as nonelectrolytes.[43,44] The conductivity results in dimethylformamide indicated that in 1×10^{-3} M solution dinitratotris(pyridine)zinc(II) was a 1:2 electrolyte and that the dinitratotris(pyridine)cadmium(II) and dinitratobis(pyridine)mercury(II) were approximately 1:1 electrolytes. Since dimethylformamide is such a good polar solvent ($\epsilon = 37$) with a high coordinating ability, these results were not totally surprising. Such behavior has been observed previously for copper(II) nitrate complexes, where the nitrates were known to be coordinated in the solid state.[44]

Because methanol is known to be a much poorer coordinating molecule than dimethylformamide and yet has a high dielectric constant ($\epsilon = 32.7$),[46] conductance measurements were run in this solvent. In all cases except tetranitratotris(pyridine)dicadmium(II), the molar conductances ranged between the values for a typical 1:1 and 1:2 electrolyte. In the former case the value was greater than that for a 1:2 electrolyte. This was not actually anomalous behavior because

the molecular formulation for this compound was that of a dimeric species; hence if the molecule completely dissociated in the solvent, the molar conductance would theoretically be considerably higher than that for a 1:2 electrolyte.

Because in many cases the molar conductances appeared to be intermediate in value between 1:1 and 1:2 electrolytic behavior, it was felt that the compounds might in fact be behaving as weak electrolytes. To check on this possibility, the molar conductances were determined as a function of concentration. The results of this study are summarized in Figures 4 and 5.

For typical strong electrolytes a plot of molar conductance vs the square root of concentration should give an approximately linear curve, and a similar plot for a weak electrolyte shows a rapid increase in molar conductance at higher concentrations.[47] The plots of molar conductance for all of the complexes in both methanol and dimethylformamide indicated that indeed all of the complexes behave as typical weak electrolytes.

The weak electrolytic behavior was a good indication that the complexes in the solid state contain metal-nitrate covalent bonds, and that concentrated solutions of the complexes are a far better approximation to their solid state configuration than are dilute solutions.

G. Molecular Weight Determinations.

Molecular weight determinations were run on 0.1 $\underline{M}$ solutions of dinitratotris(pyridine)zinc(II), dinitratotris-

(pyridine)cadmium(II), and dinitratobis(pyridine)mercury(II) in dimethylformamide. The results obtained are summarized in Table VI (p 34).

The molecular weight of the zinc(II) complex was found to be 478, which is in good agreement with the formulation of the complex as a monomeric species. The molecular weight of the cadmium(II) complex was determined to be 7640, which indicates that the complex is undoubtedly polymeric. Polymeric cadmium(II) complexes are very common,[7,16] so this result is not at all surprising.

The molecular weight of the mercury(II) complex was determined to be 129 (theor. mol wt = 483 for a monomer). This value is very low and therefore deserves some comment. An observed molecular weight of 129 indicated that the complex had dissociated into about four species. Since conductivity measurements indicated that the complex is a weak electrolyte in dimethylformamide, the dissociation probably involved cleavage of all the metal-pyridine bonds and cleavage of half of the metal-nitrate bonds. Cleavage of the metal-pyridine bonds seemed somewhat surprising in light of the high thermal stability of the complex, although thermal stability and properties in solution are not necessarily related. The low molecular weight also indicated that the complex was probably not polymeric, because were the molecule polymeric, the molecular weight should have been much higher even if pyridine were released from the complex.

H. X-Ray Powder Pattern Photographs.

X-Ray powder pattern data on all of the complexes are summarized in Tables VII-XIV (pp 36-43). Because of the complexity of the powder photographs, no attempt was made to determine the unit cell for any of the molecules.

The powder diffraction patterns for dinitratotris-(pyridine)zinc(II), dinitratotris(pyridine)cadmium(II), and dinitratobis(pyridine)mercury(II) suggested that the complexes might well be monoclinic. A monoclinic structure would not be unreasonable for the group II-B metal complexes, since such structures have been previously reported.[48,49]

The X-ray powder patterns of dinitratobis(pyridine)-zinc(II) and tetranitratotris(pyridine)dicadmium(II) were very different from those of their parent compounds. This lent further support to the contention that these were unique compounds.

The powder patterns of the trisolvates of zinc(II), cadmium(II), and mercury(II) complexes, although quite similar to those of their parent compounds, were sufficiently different to conclude that the trisolvates were unique. Basic changes in the powder patterns would not have been expected for complexes containing only adsorbed pyridine, and so this possibility is ruled out.

I. Infrared Analyses (4000-400 cm^{-1}).

Gill et al.[50] found that a majority of the absorptions attributed to complexed pyridine were nearly the same as those of the free base, the exceptions being the vibrations 6(a),

16(b), and 8(a). The two most diagnostic of these are the in-plane deformation mode, 6(a), and the out-of-plane deformation mode, 16(b), of the aromatic ring.

In the free base these peaks show up at 602 and 404 cm^{-1}, respectively. When the base is complexed, the two peaks are both shifted to higher energy. This phenomenon is quite characteristic of coordinated pyridine, and has been well documented by various workers.[8,9,51]

Table XV (p 45) lists the in-plane and out-of-plane deformation frequencies for the complexes. In every case both of the absorptions are shifted to a considerably higher frequency. Only in the case of the trisolvated complexes were absorptions due to the free base observed in the spectra. In these cases both peaks were moderately strong and indicated that two unique types of pyridine are present in the complexes. Thus it was logical to conclude that with the exception of the trisolvates, all of the other molecules contain only coordinated pyridine, and in the case of the trisolvates both coordinated and uncoordinated pyridine are present.

A second set of bands in the complexes are those ascribable to the nitrate groups. Gatehouse et al.[52] and numerous other workers[3,4] have shown that it is possible to distinguish between ionic and coordinated nitrate groups by the infrared absorption spectra of the nitrate groups.

In going from an ionic nitrate group to a coordinated nitrate group, the symmetry is reduced from D_{3h} to C_{2v}. This decrease in symmetry is accompanied by a loss in the degeneracy of the ν_3 and ν_4 bands of the ionic nitrate. Gatehouse[52] has

studied the spectra of a number of transition metal nitrates, and has made the following assignments for ionic and covalent nitrate groups:

Ionic Nitrates

ν_1 NO stretch, 1050 cm^{-1}

ν_2 nonplanar deformation, 831 cm^{-1}

ν_3 NO$_2$ stretch, 1390 cm^{-1}

ν_4 NO$_2$ bend, 720 cm^{-1}

Covalent Nitrates

ν_1 NO$_2$ symmetric stretch, 1290-1253 cm^{-1}

ν_2 NO stretch, 1034-970 cm^{-1}

ν_3 NO$_2$ symmetric bend, not observed

ν_4 NO$_2$ asymmetric stretch, 1531-1481 cm^{-1}

ν_5 NO$_2$ asymmetric bend, not observed

ν_6 nonplanar deformation, 800-781 cm^{-1}

The most definitive change in going from an ionic to a covalently bonded nitrate group is the splitting of the NO$_2$ stretching band (ν_3) into two absorption bands (ν_1 and ν_4). Furthermore, the NO stretching and nonplanar deformation bands are shifted to lower wave number. It should be noted here that whether the nitrate is monodentate, bidentate, or bridging, the point group symmetry remains the same.

It is therefore not possible to distinguish between these three modes of bonding using only infrared spectroscopy.

Bullock[53] and Curtis[55] have found it possible to distinguish between monodentate and bidentate bonding using combination bands, but this method is not practical with pyridine complexes because the spectra are too complex. An alternate method of resolving this problem was found in the simultaneous use of infrared and Raman spectroscopy. Using this method, Addison and coworkers[54] have found it possible to distinguish between monodentate and bidentate groups in tin(IV) nitrate, titanium(IV) nitrate, and vanadium(V) oxide trinitrate.

The nitrate group absorptions for the zinc(II), cadmium(II), and mercury(II) complexes are summarized in Table XV. The assignments are all consistent with coordinated nitrate groups. The magnitude of the splitting between ν_4 and ν_1 is somewhat smaller than that suggested by Gatehouse,[52] but the magnitude of the splitting is consistent with values reported by other workers.[35,57] The positions of the nonplanar deformations ($813-820$ cm^{-1}) somewhat exceed the upper limit suggested by Gatehouse,[52] but the positions are consistent with the values reported by other workers.[3,4,56]

Ferraro[56] has suggested that the magnitude of the splitting between ν_4 and ν_1 might be an indication of the degree of covalent character of the nitrate bond. In methyl nitrate, where the carbon-oxygen bond should be essentially covalent, the splitting between ν_4 and ν_1 is 385 cm^{-1}. In the zinc(II), cadmium(II), and mercury(II) complexes the splitting ranged between 148 and 188 cm^{-1}, which suggested that the degree of covalent character varied somewhat with the metal ion. Other factors would have to be considered

before any quantitative interpretation could be applied to these results.

In summary, it was found that all of the zinc(II), cadmium(II), and mercury(II) complexes contain covalently bound pyridine; and, in addition, the trisolvated molecules exhibited absorption characteristic of uncoordinated pyridine. All of the complexes also contained coordinated nitrate groups, as indicated by the absorption spectra characteristic of C_{2v} symmetry. It was not possible to differentiate between monodentate, bidentate, and bridging nitrate groups using the infrared data.

J. Far-Infrared Analyses (400-33 cm^{-1}).

Until quite recently, the use of far-infrared spectroscopy as a means of ascertaining stereochemistry was quite limited. Recently, commercial far-infrared instruments have become more readily available, and with this availability a concomitant rise in their use has occurred.

Metal halide complexes have received the greatest amount of attention. Clark and coworkers[13,33] were the torchbearers in this area. Some of their work has included assignments for the t_2 stretching vibrations of the MX_4^{n-} series of anions (M = Mn, Fe, Co, Ni, Cu, Zn) and extensive studies of complexes of the type MX_mL_n, where L is a neutral electron-donor ligand.

Metal-pyridine complexes of the general formula MX_mL_n, (X = halogen) are among the most extensive series known. They include examples of complexes with the following geometries:

tetrahedral ($MX_2 \cdot 2py$), octahedral ($MX_2 \cdot 4py$, $MX_3 \cdot 3py$, and $MX_4 \cdot 2py$, for all of which _cis_ and _trans_ isomers are known), polymeric octahedral and distorted octahedral ($MX_2 \cdot 2py$, both of which contain halogen bridges), and _cis_ and _trans_ planar ($MX_2 \cdot 2py$).[13]

Ferraro and coworkers[8] have assigned the bands of the far-infrared spectra of $Zn(py)_2X_2$, $Zn(bipy)X_2$, and $Zn(terpy)X_2$ (X = Cl, Br, I) and concluded that the pyridine and bipyridyl complexes are tetrahedral, and that the terpyridyl complexes are trigonal bipyramidal. The latter assignment is in agreement with that of Corbridge.[59] Sharp and coworkers[5,7,10] have studied a wide variety of zinc(II) halide, perchlorate, and tetrafluoroborate complexes with pyridine, triphenylphosphine, γ-picoline, and quinoline. In almost all cases, where it was possible to assign a stereochemistry to the molecules, they found that the complexes exhibited a tetrahedral or pseudo-tetrahedral geometry. Graddon and coworkers[60] have published a series of papers on the stereochemistry of zinc(II) compounds. Their conclusions, after examining a large number of complexes containing large organic ligands, were that the stereochemistry of zinc(II) appeared to be determined solely by steric effects. They found that when the ligand was such that 4-coordination could be produced, then further coordination, which would alter the tetrahedral stereochemistry, did not occur. When, however, 4-coordination could not produce a tetrahedral environment around the zinc(II) ion, then 5-coordination always occurred. In general it can be said that the stereochemistry of zinc(II) complexes is dominated by a tetrahedral or

pseudotetrahedral arrangement of the ligands around the metal
ion. When, however, tetrahedral geometry is not possible or
when it simply is not present, then five-coordination seems
to be the next most favored geometry for zinc(II).

In contrast to zinc(II), the stereochemistry of cad-
mium(II) complexes is predominantly octahedral or pseudo-
octahedral. Clark[13] has found that $CdCl_2 \cdot 2py$ and $CdBr_2 \cdot 2py$
are distorted octahedral polymers. Sharp and coworkers[7] felt
that there was strong evidence for $Cd_3(py)_2Cl_6$, $Cd(py)Br_2$,
$Cd(\beta$-pic$)Cl_2$, $Cd(\beta$-pic$)Br_2$ and $Cd(\gamma$-pic$)_4Cl_2$ all being octa-
hedral. Coates and Ridley[16] investigated a large number of
cadmium(II) complexes of the formula L_2CdX_2 (X = Cl, Br) and
found in every case that the metal was in a polymeric octa-
hedral environment. Furthermore, Sharp and coworkers[20] pre-
pared a series of aniline and substituted aniline derivatives
of cadmium(II) nitrate and sulfate, and concluded that the
metal probably had an octahedral coordination.

Mercury(II) complexes, although less well studied and
characterized than the zinc(II) and cadmium(II) compounds,
tend to favor tetrahedral and octahedral geometries. Clark[13]
has shown that $HgCl_2 \cdot 2py$ and $HgBr_2 \cdot 2py$ are distorted polymeric
octahedral compounds. Coates[16] found that many mercury(II)
complexes are tetrahedral, and that this frequently occurs
through dimerization. Misra et al.[61] have shown that for a
series of aniline and disubstituted aniline complexes of mer-
cury(II) chloride, the stereochemistry is probably pseudo-
tetrahedral, although they could not rule out the possibility
of polymeric substances.

Table XVI and Figures 6 and 7 summarize the results
of the far-infrared investigation of the zinc(II), cadmium(II),
and mercury(II) complexes.

In attempting to analyze the far-infrared spectra, it
is best to consider first what would be the most reasonable
geometries for the molecules in question, for it is through
a knowledge of the geometry that some idea of the point group
symmetry of the molecule is obtained. Knowing the point group,
it is possible to predict theoretically the far-infrared spec-
trum of the molecule.

Previous data indicated that the dinitratotris(pyri-
dine)zinc(II) was a monomer in the solid state. All of the
pyridine was coordinated to the metal and the same was true
of the nitrate groups. Since the nitrate groups could func-
tion as monodentate, bidentate, or bridging ligands, the fol-
lowing possibilities seemed most reasonable: trigonal bipy-
ramidal, octahedral with one nitrate functioning as a bidentate
ligand, polymeric octahedral with bridging nitrates, and square
pyramidal. Frank and Rogers[11] have previously reported the
spectrum of this complex and assigned the bands at 220 and
204 cm^{-1} to the meta-nitrate and metal-pyridine absorptions,
respectively. The present study has found the same peaks and
assigned them in an analogous manner. In systems analogous
to this, metal-nitrate peaks have generally been found in the
range 324-220 cm^{-1}, and the metal-pyridine peaks generally
appear below 250 cm^{-1}. Peaks below 150 cm^{-1} are usually only
tentatively assigned to deformation frequencies, because mole-
cular lattice vibrations also occur in this region and it is

usually quite difficult to ascribe any particular peak to a
definite mode. In the tris(pyridine) complex under present
discussion the peak at 200 cm^{-1} has been assigned to the
metal-pyridine stretch, but this peak is so broad that it is
difficult to determine whether or not other peaks were hidden
or masked by this broad band. The appearance of just one M-O
stretch and one M-N stretch does not allow for any type of
definitive assignment of stereochemistry to the complex. It
can be said, however, that the appearance of only two peaks
commonly occurs for both octahedral and trigonal bipyramidal
molecules. Therefore, the most that can be concluded from
the far-infrared data for this molecule is that the spectrum
is not inconsistent with either octahedral or trigonal bipy-
ramidal geometry. Considering the previous discussion, the
most reasonable structural assignment for this molecule would
be either trigonal bipyramidal, or octahedral with a bidentate
nitrate group. Square pyramidal is ruled out because this
structure has been found only in systems in which the organic
ligand forces the geometry; polymeric octahedral is ruled out
because such a structure would be inconsistent with the mole-
cular weight and conductivity measurements. The trigonal
bipyramidal and octahedral structures are both consistent with
all other available data, but it is not possible to distinguish
between these two possibilities.

Dinitratotris(pyridine)cadmium(II) shows two major
peaks in the far-infrared. The higher of these at 190 cm^{-1}
was tentatively assigned to the metal-nitrate stretch, and
the peak at 160 cm^{-1} was assigned to the metal-pyridine

stretch. In both cases these peaks appear very low for the absorptions to which they have been assigned. Frequently, metal-nitrogen stretching frequencies cannot be found in the far-infrared because they are located too low. For these reasons it was felt that these two peaks could give little unequivocal information. The only two reasonable geometries for this compound are octahedral and polymeric octahedral. This is based upon both the history of cadmium(II) complexes and the information which has been obtained on the molecule in this work. The molecular weight determination indicated that the molecule is polymeric, and the stoichiometry also suggests an octahedral geometry. Since a monomeric octahedral geometry can thus be fairly well eliminated, this leaves only a polymeric octahedral geometry for the molecule. These same arguments also hold true for the tetranitratotris(pyridine)-dicadmium(II). It is therefore suggested that both dinitrato-tris(pyridine)cadmium(II) and tetranitratotris(pyridine)di-cadmium(II) are distorted octahedral polymers, where bridging occurs by means of the nitrate groups.

As has been previously discussed, the preferred stereo-chemistry for zinc(II) and mercury(II) complexes is tetrahedral. For a tetrahedral molecule of the general formula MX_2L_2 the point group is C_{2v}. A molecule containing this symmetry should have two M-X stretching frequencies (a_1 and b_1) and two M-L stretches (a_1 and b_2), and the remaining five vibra-tions should involve X-M-X and L-M-L bends and deformations.[5] The spectra for dinitratobis(pyridine)zinc(II) showed peaks at 305 and 285 cm^{-1}, which were assigned to the M-O stretching

modes. The peaks at 250 and 210 cm^{-1} were assigned to the M-N stretching modes. Although highly tentative, the poorly resolved peak between 190 and 160 cm^{-1} could be assigned to the metal-oxygen and metal-pyridine deformations. In dinitratobis(pyridine)mercury(II) the peaks at 303 and 248 cm^{-1} were assigned to the M-O stretching vibrations, and the peaks at 220 and 165 cm^{-1} were assigned to the metal-pyridine stretches. The peaks at 130 and 110 cm^{-1} were tentatively assigned to metal-pyridine and metal-nitrate deformations respectively.

The assignments just discussed are consistent with the assignments of previous workers for metal pyridine complexes of C_{2v} symmetry. The assignments are also in agreement with the expected geometry for zinc(II) and mercury(II) complexes of the formula ML_2X_2. It is concluded, therefore, that the zinc(II) and cadmium(II) bis(pyridine) complexes are monomeric, pseudotetrahedral molecules with C_{2v} symmetry.

K. Structure of the Complexes.

Implicit in the formulation of a complex in brackets ([ ]) is the fact that all ligands contained therein are coordinately bonded to the metal. Throughout this manuscript the complexes studied in this work have been represented with brackets. The reasons for such formulations will now be presented, making liberal use of the conclusions arrived at from the experimental data.

1. Dinitratotris(pyridine)zinc(II).

The infrared and far-infrared spectra of this complex indicated that all of the pyridine in the molecule was coor-

dinatively bonded, and that the nitrate groups were also.
The molecular weight and conductance data indicated that the
complex was a monomer in the solid state. From these data
it was not possible to distinguish between five- and six-coor-
dination. Therefore, the structural possibilities for a
zinc(II) complex containing five ligands and the possibility
for bidentate bonding were considered. Knowing the structural
history of zinc(II), the conclusion was drawn that the com-
plex was either trigonal bipyramidal, or octahedral through
a bridging nitrate group, since these are the preferred stereo-
chemistries for such a complex.

2. Dinitratobis(pyridine)zinc(II) and Dinitratobis(pyridine)-
mercury(II).

The infrared and conductance data on these complexes
indicated that both the pyridine and nitrate groups were co-
ordinated to the metal ion. Far-infrared data indicated that
the complexes were pseudotetrahedral and belonged to the C_{2v}
point group. The complexes were therefore assigned a pseudo-
tetrahedral geometry with both the pyridine and nitrate groups
functioning as monodentate ligands.

3. Dinitratotris(pyridine)cadmium(II) and Tetranitrato-
tris(pyridine)dicadmium(II).

The infrared spectra of these compounds indicated that
both the pyridine and nitrate groups were coordinated to the
central metal ion. The conductance and molecular weight data
indicated that the dinitrato complex was polymeric. The far-
infrared data suggested that the complexes might be octahedral.
The X-ray powder pattern of the tetranitrato complex was

completely different from that of the parent compound, which lent support to the contention that the compound was a unique entity. Based upon these data and the fact that cadmium frequently forms polymeric octahedral compounds, the molecules were assigned a polymeric distorted octahedral geometry with bridging through nitrate groups.

4. The Trisolvate Complexes.

The infrared spectra of these compounds indicated that the nitrate groups were coordinated. The infrared also indicated the presence of both coordinated and uncoordinated pyridine. The ease and stoichiometric manner in which three moles of pyridine were lost from these complexes indicated that the three pyridines were equivalent and uncoordinated, not simply adsorbed surface pyridine. The X-ray powder patterns of the complexes indicated that their structures were different from those of their parent compounds. This also lent support to the contention that the three moles of pyridine were not simply adsorbed surface pyridine, but instead were an intimate part of the lattice structures. The stereochemistries of the molecules were therefore analogous to those of their parent compounds, but with an additional three moles of crystal pyridine.

IV. SUMMARY

The present study has been an investigation of the complexes formed between pyridine and the anhydrous metal nitrates of zinc(II), cadmium(II), and mercury(II). Pyridine complexes containing 2, 3, and 6 molecules of the base were prepared for zinc(II) nitrate. Complexes containing 1.5, 3, and 6 molecules of pyridine were prepared with cadmium(II) nitrate, and compounds containing 2 and 5 molecules of pyridine were prepared with mercury(II) nitrate.

The molecules were studied using differential thermal analysis, thermogravimetric analysis, mass spectrometry, molecular weight measurements, magnetic measurements, ultraviolet and visible spectroscopy, conductance measurements, X-ray diffraction, and infrared spectroscopy. A combination of the data from these analyses led to the following stoichiometries and tentative structure assignments for the compounds in the solid state:

$[Zn(py)_3(NO_3)_2]$: A complex having either trigonal bipyramidal or octahedral geometry with one nitrate group monodentate and the second either mono- or bidentate.

$[Zn(py)_2(NO_3)_2]$: A complex having tetrahedral geometry with monodentate pyridine and nitrate groups.

$[Zn(py)_3(NO_3)_2] \cdot 3py$: A complex having either trigonal bipyramidal or octahedral geometry with an additional three moles of crystal pyridine.

$[Cd(py)_3(NO_3)_2]$: A polymeric, distorted octahedral complex having bridging nitrate groups.

$[Cd_2(py)_3(NO_3)_4]$: A polymeric, distorted octahedral complex having bridging nitrate groups.

$[Cd(py)_3(NO_3)_2] \cdot 3py$: A polymeric, distorted octahedral complex having bridging nitrate groups and an additional three moles of crystal pyridine.

$[Hg(py)_2(NO_3)_2]$: A pseudotetrahedral complex having monodentate nitrate and pyridine groups.

$[Hg(py)_2(NO_3)_2] \cdot 3py$: A pseudotetrahedral complex having monodentate nitrate groups and three moles of crystal pyridine.

V. LIST OF REFERENCES

1. J. R. Wasson, K. K. Ganguli, and T. Theriot, *J. Inorg. Nucl. Chem.*, 29, 2807 (1967).

2. G. Beech, C. T. Mortimer, and E. G. Tyler, *J. Chem. Soc.*, A, 925 (1967).

3. R. V. Biagetti and H. M. Haendler, *Inorg. Chem.*, 5, 383 (1966).

4. R. V. Biagetti, W. G. Bottjer, and H. M. Haendler, *ibid.*, 5, 379 (1966).

5. J. Bradbury, K. P. Forest, R. H. Nuttall, and D. W. A. Sharp, *Spectrochim. Acta*, 23, 2701 (1967).

6. P. B. Bowman and L. B. Rogers, *J. Inorg. Nucl. Chem.*, 28, 2215 (1966).

7. J. A. Allan, D. H. Brown, R. H. Nuttall, and D. W. A. Sharp, *J. Chem. Soc.*, A, 1031 (1966).

8. C. Postmus, J. R. Ferraro, and W. Wozniak, *Inorg. Chem.*, 6, 2030 (1967).

9. N. S. Gill and H. J. Kingdon, *Aust. J. Chem.*, 19, 2211 (1967).

10. D. H. Brown, R. H. Nuttall, J. McAvoy, and D. W. A. Sharp, *J. Chem. Soc.*, A, 892 (1966).

11. C. W. Frank and L. B. Rogers, *Inorg. Chem.*, 5, 615 (1966).

12. N. Logan and W. B. Simpson, *Spectrochim. Acta*, 21, 857 (1965).

13. R. J. H. Clark and C. S. Williams, *Inorg. Chem.*, 4, 350 (1965).

14. W. R. McWhinnie, *J. Inorg. Nucl. Chem.*, 27, 2573 (1965).

15. W. W. Wendlandt and S. Iftikhar Ali, *Z. Anorg. Allg. Chem.*, 337, 6 (1965); *Chem. Abstr.*, 63, 7891b (1965).

16. G. E. Coates and D. Ridley, J. Chem. Soc., 166 (1966).

17. A. V. Babaeva and I. B. Baranovskii, Zh. Neorg. Khim.,
    4, 755 (1959); Chem. Abstr., 54, 7401h (1960).

18. N. G. Mitra and P. C. Sinha, J. Indian Chem. Soc., 27,
    29 (1950); Chem. Abstr., 44, 7180f (1950).

19. P. Pfeiffer and V. Pimmer, Z. Anorg. Allg. Chem., 48,
    98 (1906).

20. I. S. Ahuja, D. H. Brown, R. H. Nuttall, and D. W. A.
    Sharp, J. Chem. Soc., A, 938 (1966).

21. E. Bannister and F. A. Cotton, ibid., 2276 (1960).

22. F. A. Cotton, D. M. L. Goodgame, and R. H. Soderberg,
    Inorg. Chem., 2, 1162 (1963).

23. A. B. Lever, ibid., 4, 1042 (1965).

24. H. Schmidt, Z. Anorg. Allg. Chem., 271, 305 (1953).

25. P. Pfeiffer and K. Quehl, Ber., 64, 2667 (1931).

26. M. S. Novakovskii, V. N. Voinova, N. S. Pivnenko, and
    N. F. Kozarinova, Zh. Neorg. Khim., 11, 1738 (1966);
    Chem. Abstr., 65, 18143h (1966).

27. E. Ublig and V. Neubauer, Z. Anorg. Allg. Chem., 351,
    286 (1965).

28. C. C. Addison and D. Sutton, J. Chem. Soc., A, 1524 (1966).

29. C. C. Addison and D. Sutton in "Progress in Inorganic
    Chemistry", Vol. 8, F. A. Cotton, Ed., Interscience
    Publishers, New York, N. Y., 1967, p 255.

30. S. Kirschner and K. R. Magnell, "Optical Activity and
    the Pfeiffer Effect in Coordination Compounds", Advances
    in Chemistry Series, No. 62, American Chemical Society,
    Washington, D. C., 1966, pp 366-377.

31. J. I. Bullock and D. G. Tuck, J. Chem. Soc., 1877 (1965).

32. H. Grossman, Ber., 37, 1253 (1904).

33. R. J. H. Clark and T. M. Dunn, J. Chem. Soc., 1198 (1963).

34. F. A. Cotton and R. H. Soderberg, J. Amer. Chem. Soc., 85, 7402 (1963).

35. S. Buffagni, L. M. Vallarino, and J. V. Quagliano, Inorg. Chem., 3, 671 (1964).

36. S. C. Wallwork and W. E. Addison, J. Chem. Soc., 2925 (1965).

37. S. Swaminathan and S. Natarajan, Curr. Sci., 36, 513 (1967).

38. F. W. McLafferty, "Interpretation of Mass Spectra", W. A. Benjamin, New York, N. Y., 1967.

39. H. Sponer, J. Chem. Phys., 14, 101 (1946).

40. C. K. Jørgensen, Acta Chem. Scand., 11, 151 (1957).

41. E. König and H. L. Schläfer, Z. Phys. Chem., 26, 371 (1960).

42. C. K. Jørgensen, "Absorption Spectra and Chemical Bonding in Complexes", Addison-Wesley Publishing Co., Inc., Reading, Mass., 1962, pp 191-192.

43. D. J. Phillips and S. Y. Tyree, J. Amer. Chem. Soc., 83, 1806 (1961).

44. J. V. Quagliano, J. Fujita, G. Franz, D. J. Phillips, J. A. Walmsley, and S. Y. Tyree, J. Amer. Chem. Soc., 83, 3770 (1961).

45. G. R. Leader and J. R. Gomley, ibid., 73, 5731 (1951).

46. C. D. Hodgman, Ed., "Handbook of Chemistry and Physics", 41st ed, Chemical Rubber Publishing Co., Cleveland, Ohio, 1959, p 2513.

47. W. J. Moore, "Physical Chemistry", 3rd ed, Prentice-Hall, Inc., Englewood Cliffs, N. J., 1962, p 360.

48. F. W. B. Einstein and B. R. Penfold, Acta Crystallogr., 20, 924 (1966).

49. R. S. McEwen and G. A. Sim, J. Chem. Soc., A, 1552 (1967).

50. N. S. Gill, R. H. Nuttall, D. E. Schaife, and D. W. A. Sharp, J. Inorg. Nucl. Chem., 18, 79 (1961).

51. J. R. Durig, B. R. Mitchell, D. W. Sink, J. N. Willis, Jr., and A. S. Wilson, Spectrochim. Acta, 23, 1121 (1967).

52. B. M. Gatehouse, S. E. Livingstone, and R. S. Nyholm, J. Chem. Soc., 4222 (1957).

53. J. I. Bullock, J. Inorg. Nucl. Chem., 29, 2257 (1967).

54. C. C. Addison, D. W. Amos, D. Sutton, and H. H. Hoyle, J. Chem. Soc., A, 808 (1967).

55. N. F. Curtis and Y. M. Curtis, Inorg. Chem., 4, 804 (1966).

56. J. R. Ferraro, J. Inorg. Nucl. Chem., 10, 319 (1959).

57. R. V. Biagetti, Ph. D. Thesis, University of New Hampshire, Durham, N. H., 1965.

58. R. J. H. Clark and C. S. Williams, Chem. Ind. (London), 1317 (1964).

59. D. E. Corbridge and E. G. Fox, J. Chem. Soc., 594 (1956).

60. G. E. Batley and D. P. Graddon, Aust. J. Chem., 20, 877 (1967).

61. C. H. Misra, S. S. Parmar, and S. N. Shukla, J. Inorg. Nucl. Chem., 29, 2589 (1967).

62. F. J. Welcher, "The Analytical Uses of Ethylenediamine Tetraacetic Acid", D. Van Nostrand Co., Inc., Princeton, N. J., 1961, pp 149-150.

63. J. S. Fritz and G. S. Hammond, "Quantitative Organic Analysis", John Wiley and Sons, Inc., New York, N. Y., 1957, Chapter 3.

64. D. W. Kingston, M. S. Thesis, University of New Hampshire, Durham, N. H., 1960.

65. W. W. Wendlandt, Anal. Chem., 30, 56 (1958).

66. J. Lewis and R. G. Wilkins, "Modern Coordination Chemistry", Interscience Publishers, Inc., New York, N. Y., 1964, pp 400-454.

67. G. W. Smith, "A Computation of Diamagnetic Susceptibilities of Organic Compounds", General Motors Corp. Research Laboratories, Warren, Michigan, 1960, GMR-317.

68. C. V. Interrante, Inorg. Chem., 7, 943 (1968).

69. R. A. Krause and D. H. Busch, J. Amer. Chem. Soc., 82, 4830 (1960).

70. J. H. Fang and F. B. Bloss, "X-Ray Diffraction Tables", Southern Illinois University Press, Feffer and Simons, Inc., Carbondale, Illinois, 1966.

71. C. H. Kline, Jr. and J. Turkevich, J. Chem. Phys., 12, 30 (1944).

72. L. Cousin, B. J. Fox, and R. C. Lord, ibid., 21, 1170 (1953).

73. J. K. Wilmshurst and H. J. Bernstein, Can. J. Chem., 35, 1183 (1957).

74. G. J. Janz, M. T. Tait, and J. Meier, J. Phys. Chem., 71, 963 (1967).

75. G. Topping, Spectrochim. Acta, 21, 1743 (1965).

PART TWO

PRELIMINARY INVESTIGATION OF SOME OXIDATION AND COMPLEXATION

REACTIONS OF GROUP V-B METALS IN NONAQUEOUS SOLVENTS

I. INTRODUCTION

It has been known for several decades that metals could be oxidized in organic solvents.[1-4] The most significant feature of this technique is that the entire system can be kept water-free, and anhydrous coordination compounds can be prepared from the oxidized metal solutions.

It has been shown in this laboratory that a wide variety of metals are susceptible to such an oxidation,[5,6] but in most cases solvent interaction in the reaction makes the systems extremely complicated.

The objective of the present study was twofold in nature. The first objective was to find suitable solvents for the oxidation of the group V-B metals wherein solvent interaction would be precluded. The group V-B metals in their higher oxidation states tend to form oxy cations, rather than simple cations,[7,8] and oxy complexes are inevitably obtained from certain oxygen-containing, organic solvents. It seemed desirable to find a solvent(s) from which non-oxy complexes could be isolated. The only complexes of the group V-B metals which have been isolated from oxidized metals in an organic solvent have been isolated from methanol, and in this case the oxy or dioxy complexes have always been obtained.[6,9,10]

The oxidizing agents selected for this investigation were bromine and silver nitrate. The solvents selected for investigation were methanol, 1,2-dimethoxyethane, dioxane, tetrahydrofuran, and benzene. It was felt that this group

of solvents would include a wide variation of metal halide or metal nitrate solubility, acidity, and coordinating ability.

The second objective in this study was the isolation of complexes from the oxidized metal solutions. The two complexing agents selected were ammonium fluoride and pyridine. Their selection was based upon the facts that they are known to form complexes with the group V-B metals[5,9,11,13] and that characterization of these complexes would be moderately simple.

Part II of this thesis is divided into five major sections. Section I is the introduction, in which the scope and purpose of this work are discussed. Section II is a description of the actual work. This section includes a detailed description of the syntheses, elemental analyses, and instrumental analyses of the compounds. Section III presents the results, discussion of the experimental work, and conclusions obtained from the work. Sections IV and V, respectively, are a summary of the results obtained and a bibliography.

II. EXPERIMENTAL

A. Starting Materials.

Reagent grade methanol (Fisher) was dried by distillation from magnesium activated with iodine. Reagent grade pyridine (Fisher) was dried by distillation from potassium hydroxide and stored over barium oxide. Dioxane was dried by refluxing over calcium hydride for 12 hr and then distilling. The fraction coming over at 100-102° was collected. Formamide (Fisher), 1,2-dimethoxyethane (Eastman), anhydrous diethyl ether (Fisher), ammonium fluoride (Fisher), vanadium (A. D. Mackay, 20 mesh), niobium (A. D. Mackay, 20 mesh; Alfa Inorganics, Inc., powder), tantalum (A. D. Mackay, 20 mesh; Alfa Inorganics, Inc., powder), uranium (A. E. C., chips), and bismuth (J. T. Baker, powder) were used without further purification.

B. Bromination of the Group V-B Metals in 1,2-Dimethoxyethane.

Table I lists the quantities of reactants, duration of reflux, and the color of the resultant brominated solutions.

The metal was suspended in 75 ml of 1,2-dimethoxyethane in a 250-ml three-necked, round-bottomed flask fitted with a reflux condenser and an addition funnel. A solution containing 25 ml of 1,2-dimethoxyethane and the quantity of bromine indicated in Table I was added dropwise. Throughout the bromination the solution was magnetically stirred. After all of the bromine solution had been added, the mixture was refluxed for the length of time indicated in Table I. Upon

Table I

Conditions Used in the Brominations in 1,2-Dimethoxyethane

Metal Brominated	Quantity of Metal Used (mole)	Quantity of Bromine Used (mole)	Length of Reflux (hours)	Color of Brominated Solution
Vanadium (powder)	0.02	0.14	20	yellow-brown
Niobium (powder)	0.02	0.15	20	pale orange
Tantalum (powder)	0.01	0.070	20	pale yellow
Uranium (chips)	0.004	0.070	14	pale yellow

refluxing, the distillate gradually became lighter orange, indicating that the bromine was being used up.

Upon completion of the refluxing, dry nitrogen gas was bubbled into the heated reaction mixture through a gas dispersion tube until all of the excess bromine had been removed. The solution was then cooled and filtered in a dry atmosphere to remove any solid residue.

C. **Bromination of the Group V-B Metals in Formamide.**

Table II lists the quantities of reactants, total reaction time, and the color of the resultant brominated metals in formamide.

The metal was suspended in 100 ml of formamide in a 250-ml three-necked, round-bottomed flask fitted with a reflux condenser and an addition funnel. A solution containing 25 ml

Table II

Conditions Used in the Bromination in Formamide

Metal Brominated	Quantity of Metal Used (mole)	Quantity of Bromine Used (mole Br)	Total Reaction Time (hours)	Color of Brominated Solution
Vanadium (powder)	0.02	0.14	10	deep green
Niobium (powder)	0.01	0.14	18	yellow
Tantalum (powder)	0.007	0.14	20	orange
Uranium (chips)	0.005	0.14	20	deep orange

of formamide and the quantity of bromine indicated in Table II was added dropwise. The mixture was heated to 50-70° and magnetically stirred for the duration indicated in Table II.

After the reaction was completed, the mixture was heated to 100°, and dry nitrogen gas was bubbled into the mixture through a gas dispersion tube to expel any unreacted bromine. The solution was then cooled and filtered in a dry atmosphere. It should be noted that not all of these reactions proceeded to the same extent. In the cases of niobium, tantalum, and uranium, appreciable quantities of unreacted metal were recovered from the reaction mixture. Small quantities of other solids were also obtained, but these materials were not analyzed.

D. Bromination of the Group V-B Metals in Dioxane.

Table III lists the quantities of reactants, total

reaction time, and the color of the resultant brominated metal
solution in dioxane.

Table III

Conditions Used in the Bromination in Dioxane

Metal Brominated	Quantity of Metal Used (mole)	Quantity of Bromine Used (mole)	Total Reaction Time (hours)	Color of Brominated Solution
Vanadium (powder)	0.04	0.28	12	dark brown
Niobium (powder)	0.02	0.28	12	orange
Tantalum (powder)	0.01	0.40	12	yellow
Uranium (chips)	0.004	0.28	14	yellow

The metal was suspended in 100 ml of dry dioxane in
a 250-ml three-necked, round-bottomed flask fitted with a re-
flux condenser and an addition funnel. The concentrated bro-
mine was added dropwise through the addition funnel. Through-
out the bromination the reaction mixture was magnetically
stirred. After all of the bromine had been added, the mixture
was heated to 80-100° for the duration indicated in Table III.

After the reaction was completed, dry nitrogen gas
was bubbled into the mixture through a gas dispersion tube to
expel any unreacted bromine. The solution was then cooled
and filtered in a dry atmosphere. The bromination of vanadium
proceeds essentially to completion, but the other three metals

react to a lesser extent. In the bromination of all four metals a large excess of bromine was used. The reason for this stems from the fact that a competition between the metal and the solvent for the bromine is present. When bromine is added to dioxane, a bright orange solid immediately forms, which quickly dissolves in the bulk of the solution. This compound is probably an addition compound between the solvent and bromine. Furthermore, the solution slowly decolorizes at room temperature, indicating that bromination of the solvent occurs.

E. Oxidation of Vanadium Using Various Solvents and Oxidizing Agents.

In order to find a suitable system in which the oxidation of vanadium would lead to a single vanadium species in solution, and from which pure complexes of vanadium could be obtained, various combinations of oxidizing agent and solvent were investigated.

1. Reaction of Vanadium with Silver Nitrate in Methanol.

In a 100-ml single-necked, round-bottomed flask fitted with a silica gel drying-tube 75 ml of dry methanol was combined with 0.81 g (0.016 mole) of vanadium powder and 5.3 g (0.031 mole) of silver nitrate. The mixture was magnetically stirred at room temperature for 19 hr after which the walls of the flask were covered by a silver mirror and needles of silver metal were present in the bottom of the flask. The mixture was filtered in a dry atmosphere. The bright yellow filtrate tested positively for the presence of silver ion.

Several additional reactions similar to the one above

were investigated, wherein the molar ratio of vanadium to silver
nitrate was varied from 1:1 to 1:4. In each reaction the oxi-
dation apparently proceeded through the same series of steps.
The originally colorless solution changed to deep green, then
to deep brown and finally to bright orange. In each case the
final solution still gave a positive silver ion test with hy-
drochloric acid.

2. Bromination of Vanadium in Methanol.

In a 250-ml three-necked, round-bottomed flask fitted
with a reflux condenser and addition funnel, 100 ml of dry
methanol and 1.0 g (0.02 mole) of vanadium powder were com-
bined. While magnetically stirring, and cooling the solution
by means of an ice bath, 24 g (0.15 mole) of bromine was added
dropwise through the addition funnel. The mixture was then
refluxed for 12 hr, producing a dark yellow-brown solution.
Dry nitrogen was then bubbled into the heated reaction mixture
through a gas dispersion tube to expel any unreacted bromine.
The mixture was cooled and filtered in a dry atmosphere and
yielded a dark yellow-brown filtrate.

3. Bromination of Vanadium in Tetrahydrofuran.

In a 500-ml three-necked, round-bottomed flask fitted
with a reflux condenser and an addition funnel, 200 ml of
tetrahydrofuran and 8.1 g (0.16 mole) of vanadium powder were
combined. While magnetically stirring, and cooling the mix-
ture in an ice bath, 115 g (0.720 mole) of bromine was added
dropwise through the addition funnel. The mixture was then
refluxed for 5 hr. Subsequently, the mixture was cooled and
filtered yielding a dark yellow-brown filtrate and a small

quantity of unreacted metal.

4. Iodination of Vanadium in Methanol.

In a 250-ml three-necked, round-bottomed flask 114 g
(0.900 mole) of iodine was combined with 1.3 g (0.025 mole)
of vanadium powder in 150 ml of dry methanol. After magneti-
cally stirring the mixture for three days at room temperature,
no apparent reaction had taken place. The mixture was then
refluxed for 48 hr, which caused the formation of a small
quantity of dark brown solid in the bottom of the flask. How-
ever, most of the metal remained unreacted. If vanadium can
be oxidized by iodine in methanol, the reaction must require
more drastic conditions.

5. Bromination of Vanadium in Benzene.

In a 250-ml single-necked flask 150 ml of dry benzene
and 1.5 g (0.030 mole) of vanadium powder were placed. Through
an addition funnel 1.5 g (0.094 mole) of liquid bromine was
added dropwise to the stirred benzene solution. A reflux con-
denser was attached to the flask and the mixture refluxed for
24 hr. The mixture was initially orange-brown and the conden-
sate deep yellow. As the refluxing proceeded, the condensate
gradually became lighter yellow with concurrent evolution of
a white gas. At the end of 24 hr the mixture was filtered and
a nearly quantitative yield of unreacted metal was recovered.
The filtrate was yellow, and when water was added to the fil-
trate the yellow color remained completely in the benzene layer.
The conclusion was that vanadium cannot be brominated in ben-
zene, and that the bromine must have reacted with the solvent
or volatilized.

6. Indirect Oxidation of Vanadium in Methanol Using
   Bismuth(III).

Since the oxidation of vanadium in methanol with silver
nitrate consistently yields a solution which still contains
silver ions, an indirect oxidation of vanadium by bismuth(III)
was attempted.

In a 250-ml Erlenmeyer flask containing 150 ml of dry
methanol, 15 g (0.070 mole) of bismuth powder and 34 g (0.20
mole) of silver nitrate were combined. The mixture was mag-
netically stirred for 1.5 hr at room temperature. The mixture
was filtered to remove the silver metal, and the filtrate gave
a negative test for silver ion.

In a 250-ml single-necked, round-bottomed flask fitted
with a reflux condenser the bismuth(III) solution was combined
with 2.3 g (0.045 mole) of vanadium powder. The mixture was
refluxed over an infrared lamp for 20 hr, resulting in a bright
yellow solution containing a copious amount of bismuth metal.
The mixture was filtered in a dry atmosphere. The yellow fil-
trate gave a positive test for the presence of bismuth(III),
so additional quantities of vanadium metal were successively
added to the mixture, and the mixture was heated over an infra-
red lamp. Before each addition of metal, the filtrate gave a
positive bismuth(III) test. A total of 17 g (0.33 mole) of
vanadium was added to the reaction mixture, and still the solu-
tion gave a positive bismuth(III) test. It is obvious that
there was some stronger oxidizing agent than the bismuth(III)
present in the solution, and so it was impossible to obtain
a pure vanadium nitrate solution by this method.

F. **Ammonium Fluoride Complexes Prepared from Group V-B Metals**
   Brominated in 1,2-Dimethoxyethane.

For the sake of brevity, metal bromide solutions in 1,2-dimethoxyethane will be abbreviated as M-DMOE-Br.

1. **Reaction of V-DMOE-Br with Ammonium Fluoride.**

Ammonium fluoride (32 g, 0.89 mole) was added to 100 ml of 1,2-dimethoxyethane in a 250-ml Erlenmeyer flask. The solution was placed on a stirrer-hot-plate and heated to 70°. Through an addition funnel, 100 ml of a V-DMOE-Br solution containing 1 g (0.02 mole) of vanadium was added dropwise to the ammonium fluoride solution. Addition of the V-DMOE-Br solution resulted in the immediate formation of a mint-green solid and the solution itself turned bright yellow. After completion of the addition of V-DMOE-Br, the mixture was stirred at 70° for 20 hr. The mixture was then cooled and filtered through a sintered-glass filter under aspirator suction. The solid was washed with 1,2-dimethoxyethane and ether and placed in an oven at 115° for two hours.

Anal. Found: F, 18.56; NH_4, 24.58; Br, 42.6.

2. **Reaction of Nb-DMOE-Br with Ammonium Fluoride.**

In a 250-ml Erlenmeyer flask 11 g (0.30 mole) of ammonium fluoride were suspended in 75 ml of 1,2-dimethoxyethane. The solution was heated to 70°. Through an addition funnel 100 ml of a Nb-DMOE-Br solution containing 2 g (0.02 mole) of niobium was added dropwise with concurrent stirring to the ammonium fluoride suspension. No immediate reaction was apparent, so the mixture was heated and stirred for 12 hr. After 12 hr the reaction mixture contained a small amount of solid.

The mixture was filtered through a sintered-glass filter under aspirator suction. The solid was washed with 1,2-dimethoxy-ethane and then ether, and was finally dried in an oven at 110° for 48 hr. The product was a pale grey powder. No analytical work was done on the compound.

3. Reaction of Ta-DMOE-Br with Ammonium Fluoride.

In a 250-ml Erlenmeyer flask 11 g (0.030 mole) of ammonium fluoride was suspended in 50 ml of 1,2-dimethoxy-ethane. The solution was heated to 70°. Through an addition funnel 100 ml of a Ta-DMOE-Br solution containing 2 g (0.01 mole) of tantalum was added dropwise to the ammonium fluoride suspension. No immediate reaction was apparent, so the heating and stirring were continued for 16 hr. After 16 hr the reaction mixture contained a small quantity of white solid. The mixture was filtered through a sintered-glass filter under aspirator suction. The solid appeared to be unreacted ammonium fluoride, so under the conditions described here, no ammonium fluoride complex of tantalum was isolated.

4. Reaction of U-DMOE-Br with Ammonium Fluoride.

To 75 ml of a saturated solution of ammonium fluoride in formamide was added dropwise 50 ml of a U-DMOE-Br solution containing 0.5 g (0.002 mole) of uranium. The mixture turned dark brown with no indication of precipitate formation. The mixture was stirred at room temperature for 12 hr. At the end of 12 hr a fine, light yellow-green precipitate was present in the flask. The mixture was filtered through a sintered-glass filter under aspirator suction, and the solid was washed with methanol and ether. The light yellow-green solid was

dried in a vacuum desiccator over silica gel. No analytical work was done on the compound.

G. **Ammonium Fluoride Complexes of Vanadium, Tantalum, and Uranium Prepared from Solutions of the Brominated Metals in Formamide.**

For the sake of brevity, metal bromide solutions in formamide will be abbreviated $M-HCONH_2-Br$.

1. **Reaction of $V-HCONH_2-Br$ with Ammonium Fluoride.**

To 50 ml of $V-HCONH_2-Br$ solution containing 0.5 g (0.01 mole) of vanadium was added 50 ml of a saturated solution of ammonium fluoride in formamide. A pale green precipitate formed immediately in the flask. The flask was placed on a stirrer-hot-plate, and heated to 70° with slow stirring. After 12 hr the mixture was filtered through a sintered-glass filter under aspirator suction. The light green solid was washed with methanol and ether, and was dried in an evacuated desiccator over silica gel.

Anal. Calcd for $(NH_4)_3VOF_5$: V, 23.58; NH_4, 25.05; F, 43.97. Found: V, 21.69; NH_4, 27.90; F, 44.7.

2. **Reaction of $Ta-HCONH_2-Br$ with Ammonium Fluoride.**

To a $Ta-HCONH_2-Br$ solution containing 1.3 g (0.0070 mole) of tantalum was added 3.6 g (0.10 mole) of finely ground ammonium fluoride. No immediate reaction was apparent, so the mixture was heated to 210°. After heating for 12 hr the mixture was cooled. The mixture still contained no solid, so 50 ml of dry methanol was added to the solution to induce precipitation. A solid settled out of solution. The mixture

was filtered through a sintered-glass filter and the solid
was washed with ether. The light grey solid was placed in
an evacuated desiccator over silica gel to complete the drying.
No analysis was performed on the compound.

3. Reaction of U-HCONH$_2$-Br with Ammonium Fluoride.

To a U-HCONH$_2$-Br solution containing 1.2 g (0.0050
mole) of uranium was added 3.6 g (0.10 mole) of finely ground
ammonium fluoride. The mixture was heated to 110° and stirred
magnetically for 6 hr. The mixture containing a small amount
of yellow solid was filtered through a sintered-glass filter
under aspirator suction, and the solid was washed with ether.
The precipitate was dried in an evacuated desiccator over silica
gel. No analytical data was obtained for the compound.

H. Ammonium Fluoride Complex of Vanadium Prepared from a
Solution of Vanadium Brominated in Dioxane.

To 100 ml of a brominated vanadium solution containing
2 g (0.04 mole) of metal was added 10 g (0.30 mole) of finely
ground ammonium fluoride. A pale green precipitate formed.
Stirring was continued at room temperature for 6 hr. The mix-
ture was filtered through a sintered-glass filter under aspira-
tor suction, and the pale green solid was washed with ether.
The solid was placed in an oven at 110° for 2 hr to complete
the drying. No analytical data was obtained for the compound.

I. Ammonium Fluoride Complex of Vanadium Prepared from a
Methanol Solution of the Metal Oxidized by Silver Nitrate.

In an addition funnel was placed 100 ml of a methanol
solution containing 0.8 g (0.016 mole) of vanadium oxidized

by silver nitrate. The vanadium solution was added dropwise to 180 ml of a saturated solution of ammonium fluoride in methanol. The mixture was stirred and as the addition continued, a bright yellow solid precipitated from the solution. The mixture was refrigerated at 0° for 12 hr to complete the precipitation. After 12 hr the mixture was filtered through a sintered-glass filter under aspirator suction in a nitrogen-filled dry-box. The solid was washed with ether and dried in an evacuated desiccator over silica gel. The final product was a gold powder.

Anal. Found: V, 26.61; F, 36.09; NH_4, 30.15.

J. Ammonium Fluoride Complex of Vanadium Prepared from a Solution of the Brominated Metal in Methanol.

A solution containing 2.6 g (0.050 mole) of vanadium brominated in 100 ml of methanol was added to 715 ml of saturated ammonium fluoride in methanol. The ammonium fluoride solution was stirred during the addition. As the addition proceeded, copious amounts of a light green solid precipitated from the solution. After all of the metal solution had been added, the liquid was decanted and an additional 400 ml of saturated ammonium fluoride in methanol was added to the solid. The mixture was digested at 50° for 48 hr. The mixture was filtered through a sintered-glass filter under aspirator suction. A pale blue, gelatinous solid was obtained, which was washed four times with methanol followed by four washings with ether. The solid was placed in an evacuated desiccator over silica gel to dry. The final product was a mint-green powder.

Anal. Found: V, 20.66; F, 41.70; NH_4, 19.41.

K.   <u>Pyridine Complexes of the Group V-B Metals Prepared from</u>
<u>Solutions of the Brominated Metals in Dioxane</u>.

Table IV lists the quantities of reactants and colors
of the pyridine adducts precipitated from dioxane solutions
of the brominated group V-B metals.

Table IV

Conditions Used in the Formation of Pyridine Complexes
of the Group V-B Metal Bromides in Dioxane

Metal Used	Quantity of Metal Used (mole)	Quantity of Pyridine Used (mole)	Color of Complex
Vanadium	0.04	0.20	dark green (oily)
Niobium	0.01	0.10	yellow
Tantalum	0.01	0.10	yellow-brown
Uranium	0.002	0.10	yellow

Dry pyridine, in the amount indicated in Table IV,
was added dropwise to a stirred solution of the metal bromide
in dioxane. The quantity of brominated metal is also indicated
in Table IV. The volume of solvent ranged between 50 and 100
ml, depending upon the particular metal used. Addition of the
pyridine resulted in immediate precipitation for each of the
metal solutions. Stirring was continued for between one and
three hours after all of the pyridine had been added. The

mixture was filtered through a sintered-glass filter under aspirator vacuum, and the solid was washed with methanol and ether.

The vanadium complex was obtained as an oily solid at this point, and attempts to recrystallize the complex met with no success. The other three complexes were obtained as fine powders and attempts to recrystallize them from a large variety of solvents were unsuccessful. In every case the complexes were either insufficiently soluble in the solvent or underwent decomposition. No attempt was made to analyze the compounds because their purity was believed to be quite low.

L. Pyridine Complex of Vanadium from a Solution of Vanadium Oxidized by Silver Nitrate.

Through an addition funnel 24 g (0.30 mole) of dry pyridine was added dropwise to a stirred solution containing 2.7 g (0.052 mole) of vanadium (oxidized by silver nitrate) in 190 ml of methanol. At the end of the addition the mixture was deep orange, but no precipitate was present. Ether was slowly added to the mixture until the solution became cloudy. The mixture was refrigerated at 0° for 12 hr. At the end of this time a rust powder had settled to the bottom of the flask. The mixture was filtered through a sintered-glass filter under aspirator suction in a dry atmosphere. The precipitate was washed four times with ether, and placed in an evacuated desiccator over silica gel. The final product was a rust-yellow powder. Attempts to recrystallize the product were unsuccessful and no analytical data for the compound were obtained.

M. **Analytical Procedures**.

   1. **Vanadium Determination**.

     Vanadium was determined volumetrically by titration of a dilute sulfuric acid solution of the sample with perman-ganate.[14] Prior to the titration, the sulfuric acid solution of the sample was heated to boiling and sulfur dioxide bubbled into the solution through a gas dispersion tube for five minutes. Nitrogen was bubbled through the solution for thirty minutes to remove any excess sulfur dioxide. The purpose of this step was to reduce all of the vanadium to the 4+ oxidation state. Addition of sodium fluoride and copper sulfate seemed to give a sharper end point.[15]

   2. **Fluoride Determination**.

     Fluoride was determined by the method of Grant and Haendler[16] where fluorosilicic acid is steam-distilled from the sample and titrated oscillometrically with standard thorium nitrate solution.

   3. **Ammonia Determination**.

     The sample was placed in concentrated sodium hydroxide solution. The ammonia was distilled into a four per cent boric acid solution and was titrated with standard 0.1 $\underline{N}$ hydrochloric acid using methyl purple as indicator.[17]

     In some cases nitrogen was determined microanalytically using a Coleman Model 29 Nitrogen Analyzer.

   4. **Bromide Determination**.

     Bromide was determined gravimetrically as silver bro-mide.[18]

N. **X-Ray Powder Diffraction Photographs**.

Powder patterns were obtained on finely ground samples in 0.3 mm glass capillaries. The patterns were taken with a 57.3 mm Philips camera using copper radiation ($\lambda = 1.5418$ Å). The interplanar spacings (d_{hkl}) were read from a Nies chart. The relative intensities were estimated visually. The powder pattern for the ammonium fluoride complex prepared from a brominated vanadium solution in 1,2-dimethoxyethane agreed well with the pattern reported by Baker[9] for ammonium penta-fluoroxyvanadate(IV). Powder patterns from all other compounds were felt to be inconclusive because the compounds were impure.

O. **Infrared Spectra**.

The spectra of the solid complexes in the 4000-500 cm^{-1} range were obtained as mulls in Nujol and Halocarbon oil using a Perkin-Elmer 337 Grating Spectrophotometer. The spectra of the complexes are not reproduced in the thesis because none of the complexes analyzed as analytically pure. All of the ammonium fluoride complexes, however, contained absorptions characteristic of the ammonium ion, and peaks in the region 1000 to 480 cm^{-1}, which are probably metal-fluoride absorptions. The pyridine complex of vanadium prepared from a solution of vanadium brominated in dioxane showed shifts characteristic of coordinated pyridine in the pyridine absorption peaks.

III. RESULTS AND DISCUSSION

A. General Considerations on the Oxidation of Metals in Organic Solvents.

For many years it has been known that metals could be oxidized in organic solvents.[1-3]

Osthoff and West[19] synthesized a large variety of metal chlorides in organic donor solvents and postulated that coordination of the donor solvent to the metal chloride plays an integral part in the oxidative process. Ducelliez and Raynaud[1] prepared metal bromides of the general formula MBr_2 (M = Co, Ni, Mn, Zn, Mg) by bromination of the metals in diethyl ether at room temperature. The intermediates $MBr_2 \cdot Et_2O$ were isolated in each case. Also, Raynaud[2] was able to isolate antimony(III) and antimony(V) bromide from the bromination of antimony in diethyl ether. In another article Raynaud[3] discusses the bromination of zinc in several polar, organic solvents. From this investigation he concluded that the solvent promotes bromination of the metal only if the solvent dissolves both bromine and the metal bromide which is formed; and then only if the solvent forms a complex with the metal bromide. He proposes a mechanism in which the bromine attacks the solvent with concomitant production of hydrogen bromide, which is the active agent in brominating the metal.

Several investigators in this laboratory have studied the bromination of transition and post-transition metals in methanol.[9,10,20-24] Although large amounts of experimental data have been obtained on the bromination process, the

mechanism is still not well understood. In an excellent discussion of the brominations in methanol Baker[9,25] concludes that further work is needed before any definitive statements can be made. Because no new data concerning the mechanism of bromination have been obtained by this author, the reader is referred to reference 25 for further information concerning this very complex system.

A second oxidizing agent which may be used in organic solvents is silver nitrate. Bottjer[5,6] investigated the reactions of a large number of metals with silver nitrate in methanol. He found that antimony, arsenic, bismuth, cadmium, cobalt, copper, iodine, lead, manganese, nickel, selenium, thallium, tin, tungsten, and zinc clearly react with silver nitrate, but the ease of oxidation varies with the different metals.

The oxidation of metals in methanol by silver nitrate is by no means a simple redox reaction. Although silver metal is always one of the products, numerous other products have also been observed. Bottjer[5] reports that the infrared spectrum of the gaseous products from the oxidation of cobalt by silver nitrate in methanol contained carbon dioxide, nitrous oxide, nitrogen dioxide, methyl nitrite, and possibly formic acid. Furthermore, when ammonium fluoride was added to methanol solutions of the group V-B metals, oxy complexes were obtained, which also indicated that some other species besides silver(I) caused the oxidation of the metals. For further discussion of the silver nitrate-methanol system, the reader is referred to the work of Bottjer[5,6].

Other organic solvents in which silver nitrate has
been used as the oxidizing agent include ethanol,[26] acetone,[27]
benzonitrile,[27] acetonitrile,[28] nitromethane,[5] and ethyl ace-
tate.[5] It should be noted that in carbon tetrachloride, a
purely nonpolar solvent, none of the metals tried by Bottjer[5]
could be oxidized.

B. Oxidation of the Group V-B Metals in Various Organic
    Solvents with Bromine and Silver Nitrate.

Because of the complexity of the bromination of metals
in methanol, several other solvents were investigated. It
was felt that a solvent containing no acidic protons might
result in different oxidation states for the metals from those
obtained in methanol. Brominations of the group V-B metals
in 1,2-dimethoxyethane proceeded to varying extents. The
bromination of vanadium was complete, but the bromination of
niobium, tantalum, and uranium proceeded to a lesser extent.
There appeared to be no stoichiometric relationship between
the quantity of bromine used and the amount of metal oxidized.
As in the case of methanol,[9] the oxidation appears to involve
a complex series of oxidation-reduction reactions. When bromine
alone is added to 1,2-dimethoxyethane, the solution slowly de-
colorizes at room temperature, and decolorization occurs ra-
pidly at higher temperatures. This indicates that bromination
of the solvent occurs. Furthermore, hydrogen bromide gas is
evolved when the metals are brominated.

Formamide appears to be a far better solvent for the
brominations than 1,2-dimethoxyethane. This is probably due

in part to the fact that formamide is an excellent coordinating agent. The bromination of vanadium, niobium, and uranium proceed essentially to completion in formamide, and the bromination of tantalum to a lesser extent. Once again, the quantity of bromine necessary to bring about complete oxidation of the metals far exceeded the amount necessary for simple bromination of the metal. Although no gases were observed in these brominations, the solvent must play an intimate role in the bromination.

The extent of bromination of the group V-B metals in dioxane decreased in going down the group. The oxidation of vanadium goes essentially to completion, while the analogous uranium reaction proceeds to only a very limited extent. Once again, the bromination is complicated by the fact that dioxane itself appears to be involved in the reaction.

The bromination of vanadium in methanol and the oxidation of vanadium by silver nitrate in methanol have both been previously discussed;[5,19] hence no further discussion of these reactions will be presented here. An attempted iodination of vanadium in methanol indicated that iodine is not a sufficiently powerful oxidizing agent in methanol to realize the oxidation. Vanadium can be brominated in tetrahydrofuran, but the reaction appears to involve participation of the solvent. The indirect oxidation of vanadium in methanol by bismuth(III) indicated that the nitrate ion and the solvent must be in part responsible for the oxidation of the metal. Large quantities of the metal in excess of the stoichiometric quantity which should have been oxidized by the bismuth(III)

were added to the solution, and complete oxidation of the metal occurred, but the solution still contained bismuth(III). Vanadium could not be brominated in benzene; this is probably due to the fact that benzene is a nonpolar, nonacidic solvent.

C. Ammonium Fluoride Complexes Prepared from Solutions of the Group V-B Metals in Various Solvents.

The objective of this author in oxidizing the group V-B metals in various solvents was to ascertain whether new complexes could be obtained from these solvents. Vanadium is known to form a wide variety of complexes. The most commonly encountered complexes involve the vanadyl (VO^{2+}) and pervanadyl (VO^{3+}) ions. For a general survey of the coordination chemistry of vanadium, the reader is referred to the review articles of Selbin[7] and Nicholls.[29]

Baker[9] was able to prepare ammonium oxypentafluorovanadate(IV), ammonium hexafluoroxyniobate(V), ammonium hexafluoroxytantalate(VI), and ammonium dioxypentafluorouranate(VI) by the addition of ammonium fluoride to the brominated metals in methanol. When silver nitrate instead of bromine was used as the oxidizing agent, Bottjer was able to obtain a niobium compound analogous to that obtained by Baker,[9] but ammonium oxypentafluorovanadate(V) instead of the vanadium product obtained by Baker.[9] Johnson[13] found that using silver nitrate as the oxidizing agent for uranium resulted in the isolation of an ammonium fluoride complex analogous to that obtained from the bromination of the metal in methanol.

Numerous ammonium fluoride complexes were prepared in

the present investigation. However, the purity of these complexes was highly questionable. For this reason only speculative conclusions concerning these complexes can be discussed.

The ammonium fluoride complex prepared from 1,2-dimethoxyethane was impure, but the analysis and X-ray powder pattern indicated that the complex was contaminated ammonium oxypentafluorovanadate(IV). The ammonium fluoride complex of niobium prepared from 1,2-dimethoxyethane was not analyzed because it appeared to be a mixture which defied purification. No tantalum complex could be isolated from 1,2-dimethoxyethane. The situation for uranium was analogous to that for niobium. A complex was isolated, but purification proved futile.

The ammonium fluoride complex of vanadium prepared from formamide appeared to be ammonium oxypentafluorovanadate(IV). Again, the fact that the product is a vanadyl compound indicates that solvent participation in the bromination is present. The uranium complex isolated from formamide appeared to be a mixture, so no conclusions can be drawn concerning this compound.

The ammonium fluoride complexes prepared from brominated solutions of vanadium in both dioxane and methanol appeared to be the ammonium oxypentafluorovanadate(IV). The ammonium fluoride complex prepared from vanadium oxidized by silver nitrate, although impure, appeared to be ammonium oxypentafluorovanadate(V).

D. Pyridine Complexes of the Group V-B Metals.

The quantity of experimental data on pyridine complexes of the group V-B metal halides and nitrates is rather meager.[11-13,30-33]

The major problem seems to be that purification of the addition products leads to decomposition of the adducts.[11]

In the present investigation numerous attempts were made to purify the products resulting from the addition of pyridine to metal bromide and nitrate solutions. The addition of pyridine to dioxane solutions of all four metal halides resulted in the isolation of addition products, but attempts to purify the products were unsuccessful. The same situation was found true for the adduct isolated from a methanol solution of vanadium which had been oxidized by silver nitrate.

E. X-Ray Powder Diffraction Data.

Because the complexes formed in this work were not pure, X-ray data were used to only a limited extent. The powder pattern for the ammonium fluoride complex prepared from a brominated vanadium solution in 1,2-dimethoxyethane agreed with the pattern reported by Baker[9] for ammonium oxypentafluorovanadate(IV).

F. Infrared Analyses of Ammonium Fluoride and Pyridine Complexes of the Group V-B Metals.

Infrared analysis was used primarily as a tool to indicate the purity of complexes. In every case, complexes isolated from formamide solutions had peaks characteristic of the solvent. This indicated that either the complexes were contaminated by solvent or that formamide was coordinated to the metals. All of the vanadium complexes had a peak between 950 and 1000 cm^{-1}. This peak has been assigned by several

workers to the vanadium-oxygen stretching frequency.[34,36]
The ammonium complexes had peaks characteristic of the ammonium ion, but frequently had additional peaks characteristic of ammonium fluoride. The pyridine complexes of vanadium, prepared from a solution of brominated vanadium in dioxane, showed shifts in the pyridine absorption which were characteristic of coordinated pyridine.[37-40]

IV. Summary

A preliminary study into the possibility of brominating the group V-B metals in 1,2-dimethoxyethane, formamide, and dioxane was conducted. In most cases the bromination was successful, but solvent participation in the reactions complicated most of the systems.

The oxidation of vanadium in several additional systems was also investigated. The oxidation of vanadium in methanol by silver nitrate, although a very complex reaction, led to a solution from which pervanadyl (VO^{3+}) complexes could be isolated. The bromination of vanadium in methanol led to a solution from which vanadyl (VO^{2+}) complexes could be isolated. The bromination of vanadium in tetrahydrofuran proceeded very nicely and led to a solution similar in color to a solution of brominated vanadium in methanol. From this observation it was concluded that vanadyl ion, or a solvent complex of the same, was probably present in the solution. The iodination of vanadium in methanol was unsuccessful, as was the bromination of vanadium in benzene. The indirect oxidation of vanadium in methanol by bismuth(III) was a complicated reaction, due to the fact that other oxidizing agents appeared to be present in the solution. This made it impossible to obtain a vanadium solution which was completely free of bismuth(III).

It was possible to obtain ammonium fluoride complexes of the group V-B metals from the brominated metals in both 1,2-dimethoxyethane and formamide. However, the lack of analytical data on these complexes made their identification very

incomplete. Purification of these complexes presented the greatest problem. Ammonium fluoride complexes prepared from brominated vanadium solution in methanol and dioxane were prepared. Indications to the effect that both complexes contained the vanadyl (VO^{2+}) ion were presented.

Pyridine adducts of the group V-B metals prepared from the brominated metals in dioxane were prepared. Infrared analyses indicated that the pyridine was coordinated to the metals, but further purification of the complexes could not be accomplished. An additional pyridine complex of vanadium was prepared from a methanol solution of vanadium oxidized by silver nitrate. The color of the complex indicated that it might contain the pervanadyl ion, but further purification of the complex was unsuccessful, so absolute identification of the complex was never realized.

V. LIST OF REFERENCES

1. F. Ducelliez and A. Raynaud, _Compt_. _rend_., 158, 576 (1914).

2. A. Raynaud, _Bull_. _Soc_. _Chim_. _Fr_., 15, 599 (1914).

3. A. Raynaud, _Compt_. _rend_., 181, 1069 (1925).

4. B. J. Hathaway and D. J. Holah, _J_. _Chem_. _Soc_., 2400 (1964).

5. W. G. Bottjer, Ph. D. Thesis, University of New Hampshire, Durham, N. H., 1963.

6. W. G. Bottjer and H. M. Haendler, _Inorg_. _Chem_., 4, 913 (1965).

7. J. Selbin, _Coord_. _Chem_. _Rev_., 1, 293 (1966).

8. E. S. Gould, "Inorganic Reactions and Structure", Holt, Rinehart and Winston, Inc., New York, N. Y., 1963, p 442-446.

9. A. E. Baker and H. M. Haendler, _Inorg_. _Chem_., 1, 127 (1962).

10. R. G. Blanchette, M. S. Thesis, University of New Hampshire, Durham, N. H., 1957.

11. D. Cozzi, _J_. _Cecconi_ _Ricerca_ _sci_., 23, 609 (1953); _Chem_. _Abstr_., 48, 3891a (1954).

12. R. G. Cavell and H. C. Clark, _J_. _Inorg_. _Nucl_. _Chem_., 17, 257 (1961).

13. R. E. McCarley and J. C. Boatman, _Inorg_. _Chem_., 2, 547 (1963).

14. W. F. Hillebrand, G. E. F. Lundell, H. A. Bright, and J. I. Hoffman, "Applied Inorganic Analysis", John Wiley and Sons, Inc., New York, N. Y., 2nd ed, 1953, p 459.

15. I. M. Issa and M. Hamdy, _Z_. _anal_. _Chem_., 174, 418 (1960).

16. C. L. Grant and H. M. Haendler, _Anal_. _Chem_., 28, 415 (1956).

17. I. M. Kolthoff and V. A. Stenger, "Volumetric Analysis", Vol. II, Interscience Publishers, Inc., New York, N. Y., 1947, p 168.

18. I. M. Kolthoff and E. B. Sandell, "Textbook of Quantitative Inorganic Analysis", 3rd ed, MacMillan Co., New York, N. Y., 1952, p 308.

19. R. C. Osthoff and R. C. West, J. Amer. Chem. Soc., 76, 4732 (1954).

20. D. S. Crocket, M. S. Thesis, University of New Hampshire, Durham, N. H., 1953.

21. D. S. Crocket, Ph. D. Thesis, University of New Hampshire, Durham, N. H., 1959.

22. D. S. Crocket and H. M. Haendler, J. Amer. Chem. Soc., 82, 4158 (1960).

23. F. A. Johnson, M. S. Thesis, University of New Hampshire, Durham, N. H., 1955.

24. H. M. Haendler, F. A. Johnson, and D. S. Crocket, J. Amer. Chem. Soc., 80, 2662 (1958).

25. A. E. Baker, Ph. D. Thesis, University of New Hampshire, Durham, N. H., 1961.

26. N. W. Fischer in "A Comprehensive Treatise on Inorganic and Theoretical Chemistry", Vol. 3, J. W. Mellor, Ed., Longmans, Green and Co., London, 1923, p 319.

27. A. Guntz and F. Martin, Bull. Soc. Chim. Fr., 7, 313 (1910).

28. H. H. Morgan, J. Chem. Soc., 123, 2901 (1923).

29. D. Nicholls, Coord. Chem. Rev., 1, 379 (1966).

30. H. L. Krauss and G. Gratz, Chem. Ber., 95, 1023 (1962); Chem. Abstr., 57, 4303 a (1962).

31. H. Funk, G. Mohaupt, and A. Paul, Z. Anorg. Allg. Chem.,
    302, 199 (1959); Chem. Abstr., 54, 8401a (1960).

32. H. Funk and W. Weiss, Z. Anorg. Allg. Chem., 296, 36 (1958).

33. R. E. McCarley and B. A. Torp, Inorg. Chem., 2, 540 (1963).

34. C. G. Barraclough, J. Lewis, and R. S. Nyholm, J. Chem.
    Soc., 3552 (1959).

35. J. Selbin, L. Holmes, and S. McGlynn, J. Inorg. Nucl. Chem.,
    25, 1359 (1963).

36. A. Sabatini and I. Bertini, Inorg. Chem., 5, 204 (1966).

37. P. C. H. Mitchell and R. J. P. Williams, J. Chem. Soc.,
    1912 (1960).

38. P. C. H. Mitchell, J. Inorg. Nucl. Chem., 21, 382 (1961).

39. R. J. M. Clark and C. S. Williams, Inorg. Chem., 4, 350
    (1965).

40. J. R. Durig, B. R. Mitchell, D. W. Sink, and J. N. Willis,
    Jr., Spectrochim. Acta, 21, 1367 (1965).

41. P. R. Murthy and C. Patel, Can. J. Chem., 42, 856 (1964).

42. J. Selbin and L. Holmes, J. Inorg. Nucl. Chem., 24, 1119
    (1962).

43. J. H. Canterford and T. A. O'Donnell, Inorg. Chem., 5,
    1442 (1966).

44. B. E. Bridgland, G. W. A. Fowles, and R. A. Walton, J.
    Inorg. Nucl. Chem., 27, 383 (1965).

45. S. Chackalackal and F. Stafford, J. Amer. Chem. Soc., 88,
    4823 (1966).

46. S. Prasad and K. N. Upadhaya, J. Proc. Inst. Chem. (India),
    32, 259 (1960).

47. C. Dijkgraaf, _J_. _Phys_. _Chem_., _69_, 660 (1965).

48. D. Brown and P. J. Jones, _J_. _Chem_. _Soc_., _A_, 247 (1967).

49. R. J. H. Clark, D. L. Kepert, and R. S. Nyholm, _ibid_., _A_, 2877 (1965).

50. R. Dutta and S. Lahiry, _Sci_. _Cult_. (Calcutta), _21_, 139 (1960).