



The synthesis and reactions of some small platinum cluster compounds
by Dong Min

A thesis submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in
Chemistry

Montana State University

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Abstract:

The study of the cis Z trans isomerization of $\text{PtCl}_2(\text{Et}_2\text{S})_2$ complex is relevant to the synthesis of certain dimeric Pt(III) complexes. Not only is Cis- $\text{PtCl}_2(\text{Et}_2\text{S})_2$ a suitable starting material for Pt(III) compounds syntheses, but Cis- $\text{PtCl}_2(\text{Et}_2\text{S})_2$ itself also functions importantly in organometallic synthesis. Detailed thermodynamic and kinetic data of the cis and trans isomers, along with x-ray crystallographic structures, are summarized. Binuclear Pt(III) compounds, which have direct metal-metal bonds have been elucidated recently and their structures have been characterized by Cotton's group. Though it has been observed that there is a structural interconversion between head to head and head to tail configuration in some of the Pt(III) compounds, there is no detailed investigation of the mechanism of this interconversion. Our interest is concerned with the synthesis and mechanistic study of these binuclear Pt(III) compounds, especially the formation and rearrangement of metal-metal bonds. Presented here is the mechanism study about this interconversion. Proton NMR is mainly used in the research. Activation entropy (forward -29 vs. reverse 16 $\text{J Mol}^{-1}\text{K}^{-1}$) and activation enthalpy (84 vs. 105 kJ Mol^{-1}) of the interconversion are calculated and explained with the results from the experiment. The mechanism of the interconversion is also postulated as a dissociative concerted reaction. A modified synthetic method results in the formation of a hydroxo-bridged Pt(II) dimeric compound and an oxo-bridged Pt(II,IV) tetrameric compound. Single crystal x-ray crystallographic information is presented, along with infrared data in support of the proposed structures. The Pt(II) compound exhibits strong hydrogen bonding between molecules and its Pt-O-H bridge bond is clearly reflected in the FTIR spectrum. The Pt(II,IV) compound shows the nonequivalent oxidation states of platinum in one molecule. Platinums in the complex are bonded to one another by oxo bridges. Three platinums show pseudo square-planar, and one platinum exhibits octahedral configuration. No such examples exist in current literature. Finally reactivity of the binuclear Pt(III) compounds are studied. Different ligands have been used for axial coordination and variation of torsion angles between two methyl planes is observed. The derivatives of the binuclear platinum(III) compounds are structurally characterized by single crystal x-ray crystallography. Both structures are new to platinum chemistry. ^{31}P NMR is also used to support the structure. It is hoped this work will be helpful in understanding the synthesis and structure of further complicated platinum compounds.

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Dong Min

A thesis submitted in partial fulfillment
of the requirements for the degree

of

Doctor of Philosophy

in

Chemistry

Montana State University
Bozeman, Montana

August 1989

D378
m66

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of a thesis submitted by

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This thesis has been read by each member of the thesis committee and has been found to be satisfactory regarding content, English usage, format, citations, bibliographic style, and consistency, and is ready for submission to the College of Graduate Studies.

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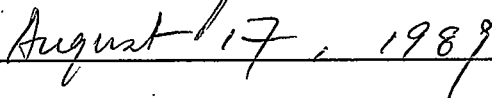
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To my dear Mom and Dad

ACKNOWLEDGEMENTS

There are so many people I would like to thank for making my stay in Bozeman pleasant.

I wish to thank Professor E. H. Abbott for his guidance and support during my graduate career.

I also wish to thank Mr. R. Larson and Professor K. Emerson for the help and technical assistance with the crystallography. I would like to thank Dr. E. S. Peterson for the helpful discussion of synthesis and teaching of NMR. I would also like to thank Dr. D. P. Bancroft for providing the Pt(III) complexes for further research. My colleagues in research, Dan Bedgood, Steven Dunham, deserve great thanks for their encouragement and help.

Finally, I express my deep gratitude for the Graduate Committee which made my trip to the United States possible.

TABLE OF CONTENTS

	Page
LIST OF TABLES	xi
LIST OF FIGURES	xiv
KEY ABBREVIATIONS	xvi
ABSTRACT	xvii
INTRODUCTION	1
Sulfate Bridged Compounds	3
Phosphate and Pyrophosphite Bridged Compound	6
Platinum Blue Complexes	9
Carboxylate and Dithiocarboxylate Bridged Compounds	12
Hydroxide and Other Bridged Complexes	15
Oxo-pyridonate Bridged Complexes	20
THE STUDY OF THE CIS TO TRANS ISOMERIZATION OF DICHLOROBIS(DIETHYLSULFIDE) PLATINUM(II) COMPLEX	27
Experimental	27
A. The syntheses of cis-PtCl ₂ (Et ₂ S) ₂ and trans- PtCl ₂ (Et ₂ S) ₂	27
B. NMR measurements on the equilibrium between cis and trans-PtCl ₂ (Et ₂ S) ₂	27
C. X-ray crystallographic determination of the structure of cis-PtCl ₂ (Et ₂ S) ₂ and trans- PtCl ₂ (Et ₂ S) ₂	29
Discussion	29
THE THERMODYNAMIC AND KINETIC STUDIES ON SOME OF THE BINUCLEAR PLATINUM(III) COMPOUNDS	43
Experimental	43
A. Syntheses of the binuclear Pt(III) compounds	43
B. NMR measurements	43

TABLE OF CONTENTS (continued)

	Page
C. NMR spectral assignments for a series of pt(III) compounds	43
D. Equilibrium constant measurement on the HH \rightleftharpoons HT interconversion	44
E. Kinetic study of the binuclear Pt(FHPy) HH \rightleftharpoons HT interconversion	60
Discussion	61
THE SYNTHESSES AND STRUCTURE DETERMINATION	
OF A GROUP OF PLATINUM COMPOUNDS	81
Experimental	81
A. Preparation of platinum compounds	81
1. Preparation of cis-PtCl ₂ (Et ₂ S) ₂ <u>1</u>	81
2. Preparation of trans-PtCl ₂ (Et ₂ S) ₂ <u>2</u>	81
3. Preparation of Ag salts <u>3</u>	81
4. Preparation of Pt ₂ (CH ₃) ₄ [(C ² H ⁵) ² S] ₂ <u>4</u>	81
5. Preparation of K ₂ [Pt ₂ (NO ₂) ₄ (OH) ₂]·1½H ₂ O <u>5</u> ..	82
6. Preparation of K ₅ [Pt ₄ (NO ₂) ₉ (O) ₃]·3H ₂ O <u>6</u>	82
7. Preparation of Pt ₂ (MHPy) ₂ (CH ₃)(Py) <u>7</u>	83
8. Preparation of [Pt ₂ (CH ₃) ₄ (MHPy) ₂ (PPh ₃)] ·2CH ₃ COCH ₃ <u>8</u>	84
9. Reaction of cis-PtCl ₂ (Et ₂ S) ₂ with pyridine <u>9</u>	84
10. Reaction of cis-PtCl ₂ (Et ₂ S) ₂ with PPh ₃ <u>10</u> ...	87
11. Reaction of cis-PtCl ₂ (Et ₂ S) ₂ with NO <u>11</u> ...	88
12. Reaction of cis-PtCl ₂ (Et ₂ S) ₂ with Ag ₂ C ₂ O ₄ <u>12</u>	88
13. Reaction of cis-PtCl ₂ (Et ₂ S) ₂ with Ag ₂ C ₂ O ₄ (modified method) <u>13</u>	89

TABLE OF CONTENTS (continued)

	Page
14. Reaction of cis-PtCl ₂ (Et ₂ S) ₂ with Ag(MHPy) <u>14</u>	89
15. Reaction of cis-PtCl ₂ (Et ₂ S) ₂ with AgNO ₃ <u>15</u> .	90
16. Reaction of K ₂ PtCl ₄ with PPh ₃ <u>16</u>	90
17. Reaction of K ₂ PtCl ₄ with Ag ₂ (C ₂ O ₄) <u>17</u>	91
18. Reaction of K ₂ Pt(NO ₂) ₄ with L-proline (C ₅ H ₉ NO ₂) <u>18</u>	91
19. Reaction of K ₂ Pt(NO ₂) ₄ with tartaric acid <u>19</u>	91
20. Reaction of K ₂ PtCl ₄ with L-proline <u>20</u>	92
21. Reaction of K ₂ Pt(NO ₂) ₄ with glycine (H ₂ NCH ₂ COOH) <u>21</u>	92
22. Reaction of K ₂ Pt(NO ₂) ₄ with D-tartaric acid <u>22</u>	92
23. Reaction of Pt ₂ (HPy) ₂ (CH ₃) ₄ (Py) ₂ with CCl ₃ COOH <u>23</u>	93
24. Reaction of Pt ₂ (HPy) ₂ (CH ₃) ₄ (Py) ₂ with CF ₃ COOH <u>24</u>	93
25. Reaction of Pt(MHPy) with CO <u>25</u>	94
26. Reaction of Pt(MHPy) with KOH <u>26</u>	95
27. Reaction of Pt(MHPy) with KCN <u>27</u>	95
28. Reaction of Pt(MHPy) with KSCN <u>28</u>	96
29. Reaction of Pt(HPy) with CH ₃ COOH <u>29</u>	96
30. Reaction of Pt(HPy) with pyrazine <u>30</u>	97
31. Reaction of Pt(Hpy) with 4-methyl pyridine (picoline) <u>31</u>	97
32. Reaction of Pt(MHPy) with pyridine <u>32</u>	98
33. Reaction of Pt(MHPy) with pyrazine <u>33</u>	98

TABLE OF CONTENTS (continued)

	Page
34. Reaction of Pt(MHPy).Et ₂ S with pyrazine <u>34</u>	98
35. Reaction of Pt(HPy) with C ₂ H ₄ <u>35</u>	99
36. Reaction of Pt(HPy) with HCl(diluted) <u>36</u> ..	100
37. Reaction of Pt(MHPy) with H ₂ S <u>37</u>	100
B. Structure Determinations	101
X-ray crystallography data collection	101
Structure solution of K ₂ [Pt ₂ (NO ₂) ₄ (OH) ₂]. 1.5H ₂ O	101
Structure solution of K ₅ [Pt ₄ O ₃ (NO ₂) ₉ . 3H ₂ O	103
Structure solution of [Pt ₂ (CH ₃) ₄ (MPy) ₂ (PPh ₃)]. 2CH ₃ COCH ₃	104
Structure solution of Pt ₂ (CH ₃) ₄ (C ₆ H ₇ NO) ₂ (C ₄ H ₄ N ₂)	106
Structure solution of cis-PtCl ₂ (Et ₂ S) ₂	109
Structure solution of trans-PtCl ₂ (Et ₂ S) ₂	111
X-ray crystallographic results	111
Structure of K ₂ [Pt ₂ (NO ₂) ₄ (OH) ₂].1.5H ₂ O	112
Structure of K ₅ [Pt ₄ (O ₃ (NO ₂) ₉].3H ₂ O	114
Structure of Pt ₂ (CH ₃) ₄ (C ₆ H ₆ NO) ₂ (PPh ₂)	118
Structure of Pt ₂ (CH ₃) ₄ (C ₆ H ₆ NO) ₂ (C ₄ H ₄ N ₂)	124
Structure of cis-PtCl ₂ (Et ₂ S) ₂	130
Structure of trans-PtCl ₂ (Et ₂ S) ₂	136
GENERAL DISCUSSION	143
Synthetic procedure	143
Structural comparisons	148

TABLE OF CONTENTS (continued)

	Page
NMR and IR studies	159
SUMMARY	162
REFERENCES CITED	165

LIST OF TABLES

Table	Page
1. Coupling constants for cis-PtCl ₂ (Et ₂ S) ₂ and trans-PtCl ₂ (Et ₂ S) ₂	40
2. ¹ H NMR assignments for Pt ₂ (CH ₃) ₄ (HPy) ₂ (Py).....	46
3. ¹ H NMR assignments for Pt ₂ (CH ₃) ₄ (HPy) ₂ (Py) ₂	48
4. ¹ H NMR assignments for Pt ₂ (CH ₃) ₄ (FHPy) ₂ (Py).....	50
5. ¹ H NMR assignments for Pt ₂ (CH ₃) ₄ (FHPy) ₂ (Py) ₂	52
6. ¹ H NMR assignments for Pt ₂ (CH ₃) ₄ (ClHPy) ₂ (Py).....	54
7. ¹ H NMR assignments for Pt ₂ (CH ₃) ₄ (MHPy) ₂ (Py).....	56
8. Equilibrium constant and thermodynamic parameters for Pt(FHPy) HH ⇌ HT	60
9. Rate constant and activation parameters for Pt(FHPy) HH ⇌ HT reaction.....	64
10. Chemical shifts of different resonances on Pt(FHPy) (HH) vs. different pyridine concentrations	79
11. Chemical shifts of different resonances on Pt(FHPy) (HT) vs. different pyridine concentrations	80
12. ¹ H and ³¹ P NMR assignments for Pt ₂ (CH ₃) ₄ (MHPy) ₂ (PPh ₃)	87
13. Crystallographic parameters for K ₂ [Pt ₂ (NO ₂) ₄ (OH) ₂]·1.5H ₂ O	103
14. Crystallographic parameters for K ₅ [Pt ₄ (O) ₃ (NO ₂) ₉]·3H ₂ O	105
15. Crystallographic parameters for [Pt ₂ (CH ₃) ₄ (MHPy) ₂ (PPh ₃)]·2CH ₃ COCH ₃	107
16. Crystallographic parameters for Pt ₂ (CH ₃) ₄ (MHPy) ₂ (C ₄ H ₄ N ₂)	108
17. Crystallographic parameters for cis-PtCl ₂ (Et ₂ S) ₂	110

LIST OF TABLES (continued)

Table	Page
18. Crystallographic parameters for trans-PtCl ₂ (Et ₂ S) ₂	112
19. Atomic coordinates and isotropic temperature factors (Å ²) with standard deviations for K ₂ [Pt ₂ (NO ₂) ₄ (OH) ₂]·1.5H ₂ O	116
20. Anisotropic thermal parameters (Å x 10 ³) with standard deviation for K ₂ [Pt ₂ (NO ₂) ₄ (OH) ₂]· 1.5H ₂ O	116
21. Bond lengths (Å) with standard deviations for K ₂ [Pt ₂ (NO ₂) ₄ (OH) ₂]·1½H ₂ O	117
22. Bond angles (°) with standard deviation for K ₂ [Pt ₂ (NO ₂) ₂ (OH) ₂]·1½H ₂ O	117
23. Atomic coordinates and equivalent isotropic temperature factors (Å ²) with standard deviations for K ₅ [Pt ₄ (NO ₂) ₉ (O) ₃]·3H ₂ O	120
24. Anisotropic thermal parameters (Åx10 ³) with standard deviation for K ₅ [Pt ₄ (NO ₂) ₉ (O) ₃]·3H ₂ O	121
25. Bond lengths (Å) with standard deviations for K ₅ [Pt ₄ (NO ₂) ₉ (O) ₃]·3H ₂ O	122
26. Bond angles (°) with standard deviation for K ₅ [Pt ₄ (NO ₂) ₉ (O) ₃]·3H ₂ O	123
27. Atomic coordinates and isotropic temperature factors (Å) with standard deviations for [Pt ₂ (CH ₃) ₄ (C ₆ H ₅ NO) ₂ (PPh ₃)]·2CH ₃ COCH ₃	126
28. Anisotropic thermal parameters (Å ² x10 ³) for [Pt ₂ (CH ₃) ₄ (C ₆ H ₅ NO) ₂ (PPh ₃)]·2CH ₃ COCH ₃	128
29. Bond lengths (Å) with standard deviation for [Pt ₂ (CH ₃) ₄ (C ₆ H ₅ NO) ₂ (PPh ₃)]·2CH ₃ COCH ₃	128
30. Bond angles (°) with standard deviation for [Pt ₂ (CH ₃) ₄ (C ₆ H ₅ NO) ₂ (PPh ₃)]·2CH ₃ COCH ₃	129
31. Atomic coordinates (x10 ⁴) and isotropic thermal parameters (Å ² x10 ³) with standard deviation for Pt ₂ (CH ₃) ₄ -C ₆ H ₅ NO) ₂ (C ₄ H ₄ N ₂)	132

LIST OF TABLES (continued)

Table	Page
32. Anisotropic thermal parameters ($\text{\AA}^2 \times 10^3$) with standard deviation for $[\text{Pt}_2(\text{CH}_3)_4(\text{C}_6\text{H}_6\text{NO})_2(\text{C}_4\text{H}_4\text{N}_2)]$	133
33. Bond lengths (\AA) with standard deviation for $\text{Pt}_2(\text{CH}_3)_4(\text{C}_6\text{H}_6\text{NO})_2(\text{C}_4\text{H}_4\text{N}_2)]$	134
34. Bond angles ($^\circ$) with standard deviation for $[\text{Pt}_2(\text{CH}_3)_4(\text{C}_6\text{H}_6\text{NO})_2(\text{C}_4\text{H}_4\text{N}_2)]$	135
35. Atomic coordinates and isotropic temperature parameters (\AA^2) with standard deviations for $\text{cis-PtCl}_2(\text{Et}_2\text{S})_2$	138
36. Anisotropic thermal parameters ($\text{\AA}^2 \times 10^3$) with standard deviation for $\text{cis-PtCl}_2(\text{Et}_2\text{S})_2$	138
37. Bond lengths (\AA) with standard deviations for $\text{cis-PtCl}_2(\text{Et}_2\text{S})_2$	139
38. Bond angles ($^\circ$) for $\text{cis-PtCl}_2(\text{Et}_2\text{S})_2$	139
39. Atomic coordinates and isotropic thermal parameters (\AA^2) with standard deviation for $\text{trans-Pt}(\text{C}_2\text{H}_5)_2\text{S})_2\text{Cl}_2$	141
40. Anisotropic thermal parameters ($\text{\AA}^2 \times 10^3$) with standard deviation for $\text{trans-Pt}(\text{C}_2\text{H}_5)_2\text{S})_2\text{Cl}_2$	141
41. Bond lengths (\AA) with standard deviation for $\text{trans-Pt}(\text{C}_2\text{H}_5)_2\text{S})_2\text{Cl}_2$	141
42. Bond angles ($^\circ$) with standard deviation for $\text{trans-Pt}(\text{C}_2\text{H}_5)_2\text{S})_2\text{Cl}_2$	142
43. Calculated Hydrogen Atom Coordinates ($\times 10^4$)	142
44. Infrared spectral results for $\text{K}_2[\text{Pt}_2(\text{NO}_2)_4(\text{OH})_2] \cdot 1.5\text{H}_2\text{O}$	150
45. Infrared spectral results for $\text{K}_5[\text{Pt}_4(\text{NO}_2)_9(\text{O})_3] \cdot 3\text{H}_2\text{O}$	154
46. Relation of the axial ligands vs. torsion angle ..	158

LIST OF FIGURES

Figure	Page
1. ^1H NMR spectrum of $\text{cis-PtCl}_2(\text{Et}_2\text{S})_2$	34
2. ^1H NMR spectrum of $\text{trans-PtCl}_2(\text{Et}_2\text{S})_2$	35
3. ^1H NMR spectra of $\text{trans-PtCl}_2(\text{Et}_2\text{S})_2$ at different temperatures	37
4. ^1H NMR spectra of decoupling of $\text{cis-PtCl}_2(\text{Et}_2\text{S})_2$...	38
5. ^1H NMR spectra of decoupling of $\text{trans-PtCl}_2(\text{Et}_2\text{S})_2$	39
6. ^1H NMR spectrum of $\text{Pt}_2(\text{CH}_3)_4(\text{HP})_2(\text{Py})$	45
7. ^1H NMR spectrum of $\text{Pt}_2(\text{CH}_3)_4(\text{HP})_2(\text{Py})_2$	47
8. ^1H NMR spectrum of $\text{Pt}_2(\text{CH}_3)_4(\text{FHP})_2(\text{Py})$	49
9. ^1H NMR spectrum of $\text{Pt}_2(\text{CH}_3)_4(\text{FHP})_2(\text{Py})_2$	51
10. ^1H NMR spectrum of $\text{Pt}_2(\text{CH}_3)_4(\text{ClHPy})_2(\text{Py})$	53
11. ^1H NMR spectrum of $\text{Pt}_2(\text{CH}_3)_4(\text{MHPy})_2(\text{Py})$	55
12. ^1H NMR spectrum of $\text{Pt}(\text{FHPy}) \text{HH} \rightarrow \text{HT}$	58
13. ^1H NMR spectrum of $\text{Pt}(\text{HPy}) \text{HH} \rightarrow \text{HT}$	59
14. $-\text{Ln}[(\text{HH})-(\text{HH})_{\text{eq}}]$ vs. time (hours) plot $\text{Pt}(\text{FHPy}) \text{HH} \rightarrow \text{HT}$ at different pyridine concentrations	68
15. $-\text{Ln}[(\text{HH})-(\text{HH})_{\text{eq}}]$ vs. time (hours) plot $\text{Pt}(\text{FHPy}) \text{HH} \rightarrow \text{HT}$ at different temperatures	69
16. Eyring plot for $\text{Pt}(\text{FHPy}) \text{HH} \rightarrow \text{HT}$	70
17. Mechanism 1 for $\text{Pt}(\text{FHPy})$ $\text{HH} \rightarrow \text{HT}$	71
18. Mechanism 2 for $\text{Pt}(\text{FHPy})$ $\text{HH} \rightarrow \text{HT}$	72
19. ^1H NMR spectrum of $\text{Pt}(\text{HPy}) \text{HT} \rightarrow \text{HH}$	78
20. ^1H NMR spectrum of $\text{Pt}_2(\text{CH}_3)_4(\text{MHPy})_2(\text{PPh}_3)$	85

LIST OF FIGURES (continued)

Figure	Page
21. ^{31}P NMR spectrum of $\text{Pt}_2(\text{CH}_3)_4(\text{MHPy})_2(\text{PPh}_3)$	86
22. ORTEP view of $\text{K}_2[\text{Pt}_2(\text{NO}_2)_4(\text{OH})_2] \cdot 1.5\text{H}_2\text{O}$	115
23. ORTEP view of $\text{K}_5[\text{Pt}_4(\text{NO}_2)_9(\text{O})_3] \cdot 3\text{H}_2\text{O}$	119
24. ORTEP view of $[\text{Pt}_2(\text{CH}_3)_4(\text{MHPy})_2(\text{PPh}_3)]$	125
25. ORTEP view of $\text{Pt}_2(\text{CH}_3)_4(\text{MHPy})_2(\text{C}_4\text{H}_4\text{N}_2)$	131
26. ORTEP view of $\text{cis-PtCl}_2(\text{Et}_2\text{S})_2$	137
27. ORTEP view of $\text{trans-PtCl}_2(\text{Et}_2\text{S})_2$	140
28. ORTEP view of molecular arrangement in $\text{K}_2[\text{Pt}_2(\text{NO}_2)_4(\text{OH})_2] \cdot 1.5\text{H}_2\text{O}$	151
29. ORTEP view of molecular arrangement of $\text{Pt}(\text{MHPy})$ with different axial ligands	157

KEY ABBREVIATIONS

Å	=	Angstroms
Et ₂ S	=	Diethylsulfide [(H ₅ C ₂) ₂ S]
Hz	=	Hertz
MHz	=	Megahertz
NMR	=	Nuclear Magnetic Resonance
ppm	=	part per million
Pt(HPy) (HH)	=	Pt ₂ (CH ₃) ₄ (C ₅ H ₄ NO) ₂ (Py)
Pt(HPy) (HT)	=	Pt ₂ (CH ₃) ₄ (C ₅ H ₄ NO) ₂ (Py) ₂
Pt(FHPy) (HH)	=	Pt ₂ (CH ₃) ₄ (C ₅ H ₃ NOF) ₂ (Py)
Pt(FHPy) (HT)	=	Pt ₂ (CH ₃) ₄ (C ₅ H ₃ NOF) ₂ (Py) ₂
Pt(ClHPy)	=	Pt ₂ (CH ₃) ₄ (C ₅ H ₃ NOCl) ₂ (Py)
Pt(MHPy)	=	Pt ₂ (CH ₃) ₄ (C ₆ H ₆ NO) ₂ (Py)
Pt(MHPy).Et ₂ S	=	Pt ₂ (CH ₃) ₄ (C ₆ H ₆ NO) ₂ (Et ₂ S)
Pt(MHPy).PPh ₃	=	Pt ₂ (CH ₃) ₄ (C ₆ H ₆ NO) ₂ (PPh ₃)
Pt dimer	=	K ₂ [Pt ₂ (NO ₂) ₄ (OH) ₂]·1½H ₂ O
Pt tetramer	=	K ₅ [Pt ₄ (NO ₂) ₉ (O) ₃]·3H ₂ O
Py	=	Pyridine
X	=	Halogen or specified function group

ABSTRACT

The study of the cis \rightleftharpoons trans isomerization of $\text{PtCl}_2(\text{Et}_2\text{S})_2$ complex is relevant to the synthesis of certain dimeric Pt(III) complexes. Not only is cis- $\text{PtCl}_2(\text{Et}_2\text{S})_2$ a suitable starting material for Pt(III) compounds syntheses, but cis- $\text{PtCl}_2(\text{Et}_2\text{S})_2$ itself also functions importantly in organometallic synthesis. Detailed thermodynamic and kinetic data of the cis and trans isomers, along with x-ray crystallographic structures, are summarized. Binuclear Pt(III) compounds, which have direct metal-metal bonds have been elucidated recently and their structures have been characterized by Cotton's group. Though it has been observed that there is a structural interconversion between head to head and head to tail configuration in some of the Pt(III) compounds, there is no detailed investigation of the mechanism of this interconversion. Our interest is concerned with the synthesis and mechanistic study of these binuclear Pt(III) compounds, especially the formation and rearrangement of metal-metal bonds. Presented here is the mechanism study about this interconversion. Proton NMR is mainly used in the research. Activation entropy (forward - 29 vs. reverse 16 $\text{J Mol}^{-1}\text{K}^{-1}$) and activation enthalpy (84 vs. 105 kJ Mol^{-1}) of the interconversion are calculated and explained with the results from the experiment. The mechanism of the interconversion is also postulated as a dissociative concerted reaction. A modified synthetic method results in the formation of a hydroxo-bridged Pt(II) dimeric compound and an oxo-bridged Pt(II,IV) tetrameric compound. Single crystal x-ray crystallographic information is presented, along with infrared data in support of the proposed structures. The Pt(II) compound exhibits strong hydrogen bonding between molecules and its Pt-O-H bridge bond is clearly reflected in the FTIR spectrum. The Pt(II,IV) compound shows the nonequivalent oxidation states of platinum in one molecule. Platinums in the complex are bonded to one another by oxo bridges. Three platinums show pseudo square-planar, and one platinum exhibits octahedral configuration. No such examples exist in current literature. Finally reactivity of the binuclear Pt(III) compounds are studied. Different ligands have been used for axial coordination and variation of torsion angles between two methyl planes is observed. The derivatives of the binuclear platinum(III) compounds are structurally characterized by single crystal x-ray crystallography. Both structures are new to platinum chemistry. ^{31}P NMR is also used to support the structure. It is hoped this work will be helpful in understanding the synthesis and structure of further complicated platinum compounds.

INTRODUCTION

Platinum, first discovered as a 50-80% alloy with gold and silver, was considered to be water-born grain in ancient times. Because of the difficulties in its separation from other materials and its high melting point, it was not until 1741 that the first pure sample of platinum was under investigation by European scientists (1).

Since then, many remarkable properties of this element have been discovered. Early ones were its strong resistance to corrosion, even under the attack of aqua regia, and its excellent electrical conductivity. As early as 1840, chemists found the metal had the ability to form complicated networks of bonds under fairly moderate conditions with various ligands. A Pt-Pt metal bond was reported in a journal at that time (2). Thereafter platinum not only interested chemists for its shining surface and value but also for its chemical activity. In recent years, the development of research on this metal has further revealed its important catalytic activity in organic synthesis and petroleum industrial processes. There is also more and more focus on the biochemical activity of platinum compounds, especially the anti-tumor properties of several of its compounds (3). Modern research is directed at determining systematic aspects of Pt chemical properties and even investigating the potential application of using platinum

clusters for electronic circuitry which could change the electronic industry dramatically (4).

Our purpose in research has centered in the area of new methods for synthesis of platinum compounds with Pt-Pt bonds. We are also interested in structure elucidation and chemical properties. Our efforts have been directed towards two objectives:

1. Synthesis of platinum dimer, trimer, tetramer cluster compounds and their structure determination.
2. Determining the mechanisms of certain platinum clusters rearrangement reactions.

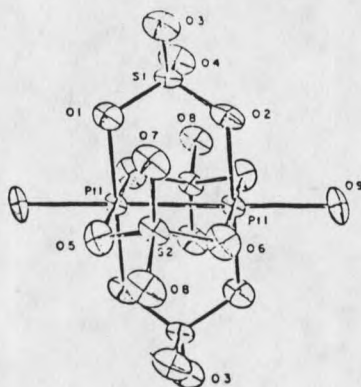
Because we are interested in making platinum compounds which have one or more Pt-Pt bonds, the basic understanding of the platinum oxidation states verses the electron configuration of the compound needs to be considered first.

Recently, a group of the platinum(III) binuclear compounds, first characterized in detail by F. Albert Cotton's group, has been shown to have a net single bond between platinum metal atoms and the $\sigma^2\pi^4\delta^2\delta^{*2}\pi^{*4}$ electronic configuration (5). Such a configuration enables this system to form two bridging ligands bonding with the metal atoms and axial bonding with appropriate monodentate ligand as is commonly seen in the Rh^{+4}_2 system (6-8) which is isoelectronic with the Pt^{+6}_2 system. Numerous examples have been characterized structurally in the Rh^{+4}_2 system.

Therefore one object of our work was to develop the methodology for the synthesis of Pt_2^{6+} groups where only a few structures are known and to extend it to the development of platinum cluster formation. Let us begin by reviewing the current state of knowledge of Pt_2^{6+} groups.

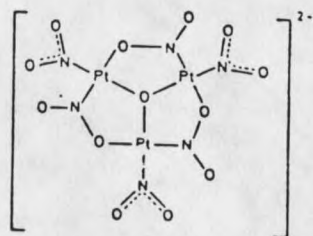
Sulfate Bridged Compounds

In 1893 Veves reported that the reaction of dilute mineral acids with $K_2[Pt(NO_2)_4]$ resulted in the formation of copper red needles (9, 10) which he formulated as $K_2H_4Pt_3(NO_2)_6O \cdot 3H_2O$. In 1905, Blondel prepared the first well-characterized compound in this category which he suggested to be a Pt(III) complex (11). In this reaction, Pt(IV) oxide was reacted with aqueous sulphuric acid and subsequently reduced by the addition of oxalic acid. At the time, Blondel formulated this Pt complex as $K[Pt(SO_4)_2] \cdot H_2O$. His work was later confirmed by Wohler and Frey who independently prepared this compound along with other related species (12). It was not until 1976, with the use of x-ray crystallography that this compound was correctly formulated as $K_2[Pt_2(SO_4)_4(H_2O)_2] \cdot 9.5H_2O$ --a binuclear Pt(III) compound [1](13).



[1]

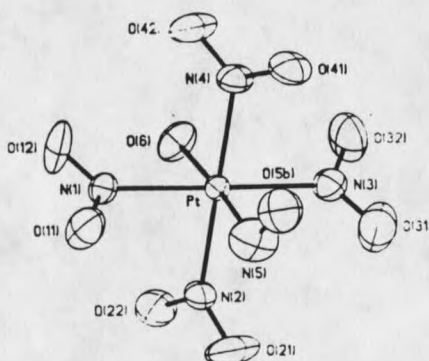
In 1977, new investigations of Vezes' red salt also reformulated the compound as $K_2[Pt_3(NO_2)_6O] \cdot 3H_2O$ [2](14).



[2]

The potassium salt $K_2[Pt_2(SO_4)_4(H_2O)_2]$ was the first structurally characterized Pt_2^{6+} binuclear complex (15-17). This work was later improved by using the reaction of $K_2[Pt(NO_2)_4]$ with H_2SO_4 in which an oxidation reaction occurs during the process. The conditions for the reaction are fairly simple. The basic requirement for this reaction is to dissolve the potassium salt with aqueous sulphuric acid followed by 10 minutes heating of the solution in an oil

bath at 353 K. Slow evaporation in vacuum results in a change of color of the solution from colorless to light blue, blue, green, yellow and, finally, when exposed to air with the addition of H₂O, a red precipitate form. In this process, each color may represent an individual compound and structure determination confirmed one of the compounds as K[Pt(NO₂)₄(NO)(H₂O)]·H₂O [3](18).



[3]

A few derivatives of the sulfato-bridged platinum compound containing neutral or anionic axial ligands were also reported such as K₂[Pt₂(SO₄)₂(OSMe)₂]·4H₂O (13). Most reactions take place at the axial position of this platinum(III) complex. Generally the Pt-Pt bond length is about 2.50-2.60 Å.

Although the reaction between K₂Pt(NO₂)₄ and H₂SO₄ was first performed about 80 years ago, the correct structure of the product was not determined until 1984 (19). Similar types of the sulfato-bridged, metal-metal bonded compounds were also seen for [Re₂(SO₄)₄(H₂O)₂]⁻⁴ and [Mo₂(SO₄)₄(H₂O)₂]⁻⁴ that were characterized in the mid 70's

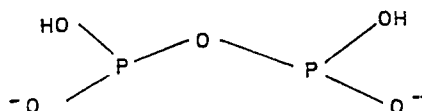
(15-16).

Phosphate and Pyrophosphite bridged complexes

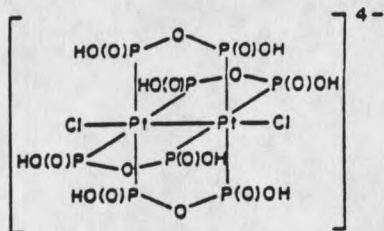
Binuclear platinum(III) phosphate compounds were discovered in 1980 (20). Their structures were determined shortly thereafter (21). The structure is very similar to that of sulfato bridged platinum complexes. The structure of the sulfate and phosphate complexes is referred to as a "lantern" structure. This lantern form represents a comparatively short metal-metal bond, four bridging ligands coordinated to the two platinum atoms and either one or two axial ligands as illustrated above [1].

A variety of derivatives has been synthesized with pyridine as an axial ligand and characterized by x-ray crystallography (22).

Another class of compounds is arrived at via an oxidation reaction of a binuclear platinum(II) complex which was synthesized from K_2PtCl_4 with bridging pyrophosphite [$H_2P_2O_5, (POP)^{-2}$] ligands in 1982. POP is the anhydride of phosphorous acid (H_3PO_3) with two oxygen ions available for coordination [4]. The formation of binuclear platinum(III) complexes with methyl iodide or halogens as oxidizing agents in the axial position was first observed [5](23-26).



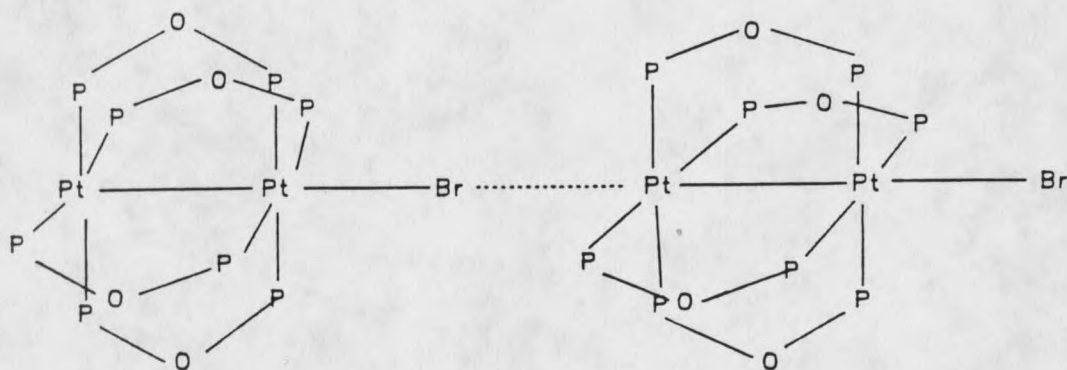
[4]



[5]

The general formula for these Pt(III) complexes is $[\text{Pt}_2(\text{POP})_4\text{X}_2]^{-4}$. They all have the lantern structures. The formation of Pt-Pt single bond apparently results from loss of the two antibonding σ electrons in $[\text{Pt}_2(\text{POP})_4]^{-4}$ in the $\sigma^2\pi^4\delta^2\delta^{*2}\pi^{*4}\sigma^{*2}$ electron configuration. The two antibonding σ electrons are transferred to the incoming X_2 molecule in $[\text{Pt}_2(\text{POP})_4\text{X}_2]^{-4}$ to form $\sigma^2\pi^4\delta^2\delta^{*2}\pi^{*4}$ electron configuration. The decrease of bond length (from 2.925 Å to 2.695 Å) supports the explanation. This interpretation is also supported by electronic absorption spectra of the complex where a higher energy, intense component has been assigned to a $d\sigma \rightarrow d\sigma^*$ transition (24).

More interesting results came from the oxidation of $[\text{Pt}_2(\text{POP})_4]^{-4}$ by bromine water in which a final product $[\text{Pt}_2(\text{POP})_4\text{Br}] \text{H}_2\text{O}$ formed [6](26).



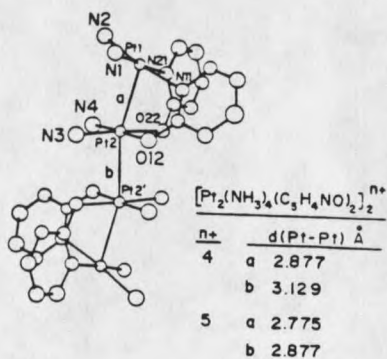
[6]

This complex has distinct semi-conductor properties. The structure showed the one dimensional packing along Pt-Pt-Br direction. This paired stacking provides the pathway for conduction. The Pt-Pt bond length is 2.793 Å and the Pt-Br distance is 2.699 Å. The longer distance between Pt-Pt in the pyrophosphite bridged complex was due to the large bite distance of the POP bridge ligands. With the use of ^{31}P and ^{195}Pt NMR, one can study the platinum-phosphine complexes which have magnetically different platinum and phosphine atoms by measuring the coupling constant and chemical shifts, as Pt-Pt coupling constants and Pt-P coupling constants are directly measured from spectra, usually from an AB pattern. With different bridging and axial ligands, the coupling constants and chemical shifts vary in magnitude; this coupling constant and chemical shift provide a way to study the interaction between the Pt ions and Pt-P atoms as well. Infrared spectra are also helpful in

studying the Pt-Pt and Pt-X stretching modes.

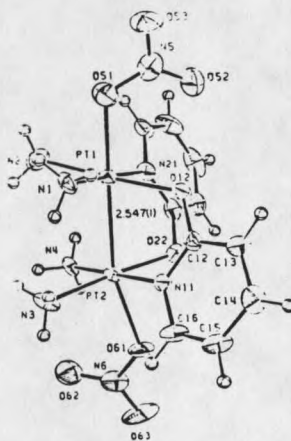
Platinum Blue Complexes

"Platinum blues" are mixed valence polynuclear Pt compounds with an intense blue absorption. The first platinum blue compound was prepared in 1908 when the German chemists Hoffman and Bugge ran the reaction of $\text{Pt}(\text{CH}_3\text{CN})_2\text{Cl}_2$ with K_2PtCl_4 and obtained a blue product with the formula $\text{Pt}(\text{CH}_3\text{CONH})_2 \cdot \text{H}_2\text{O}$ (27). Though the early platinum blue complex had historical significance, it was not until the discovery of the anti-tumor activity of the platinum blue synthesized from $\text{cis-Pt}(\text{NH}_3)_2(\text{H}_2\text{O})_2$ that there was much interest in this group of compounds. Since the discovery of the powerful anti-cancer drug $\text{cis-Pt}(\text{NH}_3)_2\text{Cl}_2$ (28-30), many platinum blue compounds have been prepared. In 1977, the first platinum blue complex was structurally characterized by x-ray crystallography. The crystals are found in the reaction of α -pyridone with $\text{cis-PtCl}_2(\text{NH}_3)_2$ in dilute HNO_3 acid solution for [7](31).



[7]

This compound had two binuclear platinum complexes coordinated together by a Pt-Pt bond. Each binuclear platinum complex had the same configuration. Two cis-ammine groups were coordinated to each Pt atom and two α -pyridone ligands bridged the two Pt atoms in a cis orientation. This platinum blue complex was further studied and it was found that the oxidation of the platinum tetramer by HNO_3 resulted in red crystals. It was characterized as cis- $[\text{Pt}_2(\text{NH}_3)_4(\text{Pyr})_2(\text{NO}_3)(\text{H}_2\text{O})]$ with a head-to-head configuration of the α -pyridone bridges. In this head-to-head form labeled as HH, platinum is bonded to both nitrogens or oxygen ions of the bridging ligands. It was later found that HH would form cis- $[\text{Pt}_2(\text{NH}_3)_4(\text{Pyr})_2(\text{NO}_3)_2]$ (HT) (head to tail configuration) with the addition of HNO_3 [8](32-33).



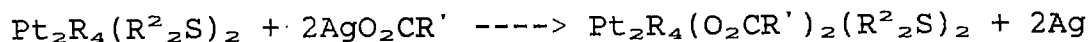
[8]

The difference between HH and HT is whether or not the Pt atoms are coordinated to both nitrogens or oxygens on the α -pyridone bridge. In the HH Pt complex, each Pt is coordinated to either both N atoms or to both O atoms on

metal and biological active ligands occur and where a lot of challenging questions are still unanswered.

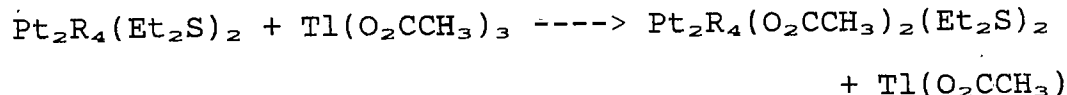
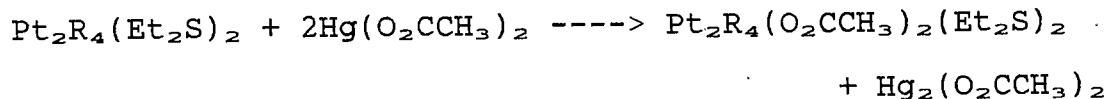
Carboxylate and Dithiocarboxylate Bridged Compounds

The first studies on the carboxylate bridged platinum(III) compound were reported in 1976 and in 1977 (35-36). Ag(I) salts oxidized platinum(II) compounds according to the following reaction:



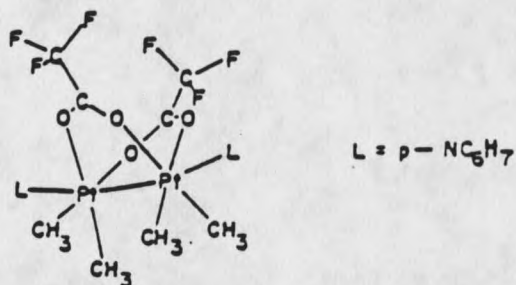
R=Ph, p-tolyl, Me, R'=Me, CF₃, R²=Et, Pr.

The series of complexes with two bridging carboxylate groups coordinated to the platinum atoms in a cis position were studied and formulated as Pt₂R₄(O₂CR')₂(R²₂S)₂. For most reactions, the starting materials were the cis-Pt(R²₂S)₂Cl₂ compounds. They react with CH₃Li to form binuclear complexes in which each Pt is bonded to two methyl groups and is bridged by two R²₂S ligands. Further oxidation by a Ag(I) carboxylate or possibly by Hg(II) or Tl(III) carboxylate salts, made these reactions proceed as follows (37):



R=CH₃, Ph, p-tolyl

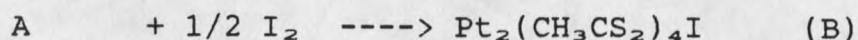
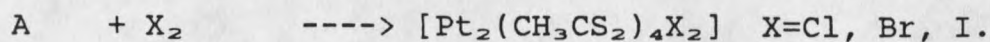
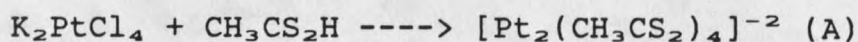
In 1978, a binuclear Pt(III) complex was fully characterized by x-ray crystallography [10](38).



[10]

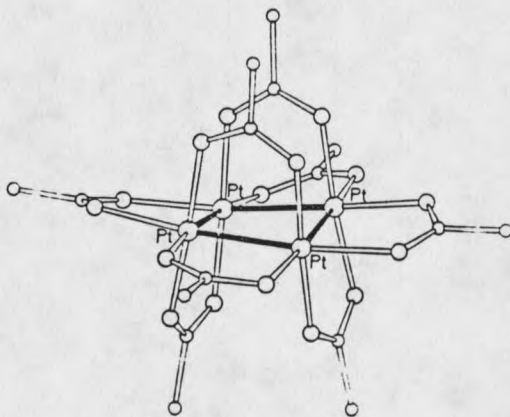
The structure of the complex was similar to the α -pyridone bridged complex with two trifluoroacetate ligands bridging the two platinum atoms and a net single bond forming in between (Pt-Pt bond length 2.557 Å). Each platinum atom was coordinated by two methyl groups in a cis orientation and two 4-Methylpyridine groups in the axial position. There was a torsional twist along the N-Pt-Pt-N direction by 26 degree from linearity due to methyl steric repulsions.

Dithiocarboxylate ligands also bridge two platinum atoms forming similar types of compound (39).



The distance between the Pt-Pt was 2.677 Å and compound B was proven to have semiconductive properties. It was suggested that this property was caused by the stacking of the regular units along Pt-Pt-I direction as a pathway to transport the electrons.

As the studies on carboxylate bridged compounds increased, more new compounds were structurally characterized and different synthetic routes were explored. In 1976, a tetrameric carboxylate complex was studied. It was suggested that its structure was a planar square of four platinum(II) atoms bridged by eight acetate ions [11](40).

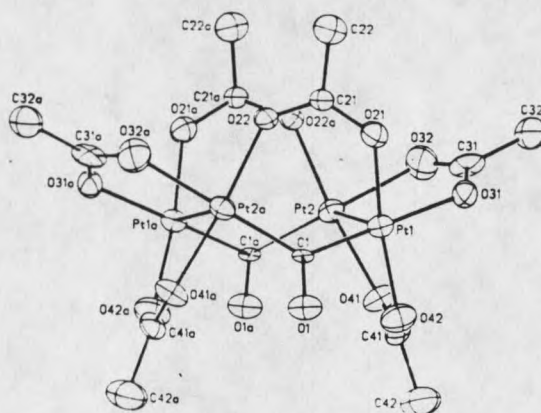


[11]

There was direct bonding between Pt(II)-Pt(II) in the square so as to create pseudo-octahedral coordination around each platinum(II). X-ray crystallography confirmed this structure. Such an arrangement of bridge ligands in this complex led us to study more complex carboxylate ligands. Efforts were made to synthesize structure-similar bridging

compounds using $K_2Pt(NO_2)_4$, K_2PtCl_4 and even *cis*- $PtCl_2(Et_2S)_2$ with tartaric acid ($C_4O_6H_6$) and Ag(I) oxalate salt, etc.

Derivatives of the carboxylate bridged platinum(II) tetramer were studied and a carbonyl bridged compound was discovered and characterized structurally [12](18).



[12]

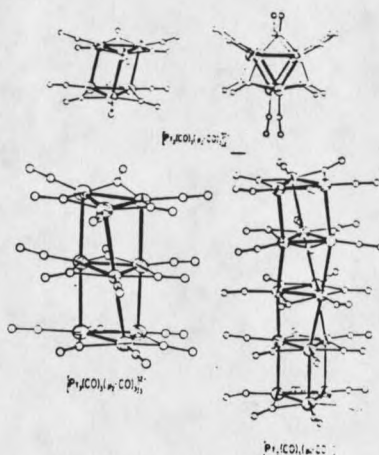
Studies showed that this platinum complex was stable in air and the Pt tetramer frame kept intact under the various ligand substitutions. IR and XPS data indicated the postulated structures when a single crystal was impossible to obtain (18).

Hydroxide and Other Bridged Complexes

In 1974, Russian chemists claimed a reaction product ($K_2Pt(NO_2)_4 + H_2SO_4$ under $100^\circ C$) $K_2(H_3O)[Pt_2(SO_4)_4(H_2O)(OH)]$ formed. While this compound was filtered the residue was extracted by acetone (41). They formulated the final product as peroxide O_2^{-2} bridged $[Pt_2(O_2)_2(OH)_2(H_2O)_2]_n$.

KHSO_4 . Unfortunately the work was not verified by X-ray crystallography and the structure was totally inferred from infrared spectroscopy, microanalysis and potentiometric titration.

In 1974, Italian chemists reported the synthesis and structures of platinum carbonyl clusters $[\text{Pt}_3(\text{CO})_3(\mu\text{-CO})_3]_n^-$ ² (n=2, 3, 4, 5)[13](42).

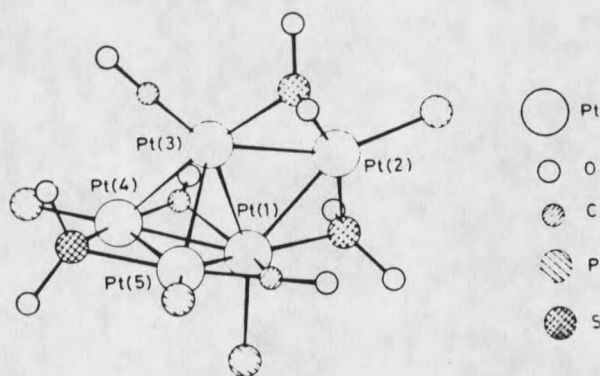


[13]

This series of platinum clusters is of particular interest, because it displays a basic $\text{M}_3\text{L}_3(\mu\text{-X})_3$ type building block with direct metal-metal interactions. The 2.66 Å intracluster Pt-Pt distances are within the expected Pt-Pt single bond range. The intercluster Pt-Pt distances averaged 3.03-3.05 Å which indicated the metal-metal interactions were not very strong and the whole stacking was twisted. This kind of cluster represented an approach to the synthesis of a unique type of one dimensional metal cluster polymer with potential desirable conductivity.

In recent years, another kind of cluster was synthesized

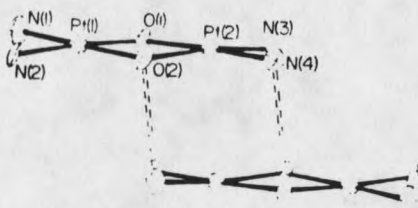
and the structure was characterized as $[\text{Pt}_5(\text{CO})(\mu\text{-CO})_2(\mu\text{-SO}_2)_3 - (\text{PPh}_3)_4]$ [14](43).



[14]

The unbridged Pt-Pt bond lengths radiating from Pt(3) in the complex averaged 2.78 Å. The cluster might be more correctly described in terms of two orthogonal triangular-clusters which share a common metal atom. The investigator involved also indicated that SO_2 was a better sigma donor than CO and CO was a better pi acceptor electronically. Hence this complex not only had a CO bridging bond but also had a SO_2 bridging bond between platinum atoms. The synthesis of the cluster required passing SO_2 gas through a toluene solution of $\text{Pt}(\text{C}_2\text{H}_4)(\text{PPh}_3)_2$. The product was formulated as $\text{Pt}_3(\text{SO}_2)_3(\text{PPh}_3)_3$ which was the starting material for synthesis of the platinum cluster compound $\text{Pt}_5(\text{CO})(\mu\text{-CO})_2(\mu\text{-SO}_2)_3(\text{PPh}_3)_4$ (44). The diversity of the SO_2 bridged platinum complexes opened up an entirely different chemistry. The lability of the SO_2 ligand may be useful synthetically.

Several platinum coordination compounds with hydroxide bridges have been isolated and characterized [15](45).

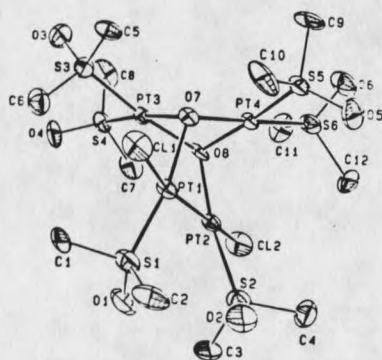


[15]

The structures of the complexes showed that the two OH groups bridged the two platinum atoms in a cis fashion forming two square-planar configurations. Each platinum dimer in the unit cell was stacked over another. Strong interaction between each layer was most likely caused by hydrogen bonding. The dimer unit was essentially planar although a twist of the planes and the distortion such that Pt(2)(a) and Pt(2)(b) moved out of the square planes away from each other could be seen. The interdimer distance was 2.81 Å (a and b indicate different molecules).

The synthesis was strongly dependent upon controlling the pH of the solvent and crystal formation only occurred in basic solution. Infrared spectroscopy showed a Pt-O-H bending mode which indicated that the compound was hydroxide bridged. Similar syntheses also resulted in the formation of hydroxide bridged platinum trimer and tetramer (46-47). The platinum trimer had roughly C_{3v} symmetry. All the

bridging hydroxide groups lay on the same side of the three platinum plane. Each platinum atom and its ligands formed an essentially planar configuration error. The platinum tetramer might be visualized as consisting of a tetrahedral core of oxygen atoms, with platinum atoms bridging four of the six edges of the tetrahedron. The four Pt atoms defined a plane and were located approximately on the corner of a square. Coordination around each platinum atom was square planar. An oxo-bridged platinum complex was only recently reported (48) and the structure was characterized by crystallography [16]. This Pt(I)-Pt(II) complex contained a metal-metal bonded diplatinum(I) unit. One $\text{Pt}_2\text{Cl}_2(\text{DMSO})_2$ unit fused into a dimeric $\text{Pt}_2\text{O}_2(\text{DMSO})_4$ unit by the formation of two μ -oxo bridges. The geometry about each platinum atom was nearly square planar.



[16]

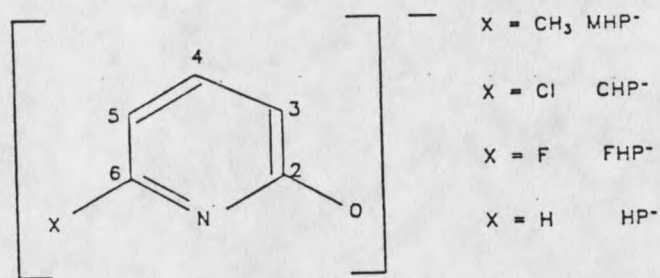
Oxo-Pyridonate Bridged Complexes

Some α -pyridone bridged platinum complexes have been discussed. The platinum blue compounds were chiefly prepared by either chemical or electrochemical oxidation of the mixed-valent platinum compounds (49-51). However, the syntheses for these products have been found to be non-repeatable or the yields too low to represent a systematic route for obtaining them. Precursors for these complexes tend to be unstable in air and do not have good solubility as well. A research group led by F. A. Cotton has synthesized a series of platinum(III) binuclear compounds bridged by a series of oxopyridonate ligands in high yields. These Pt(III) complexes are stable in air and soluble in the organic solvents. The syntheses are based on Vrieze's method (35) in which platinum(II) compounds react with Ag(I) carboxylate to form carboxylate bridging bonds between the two platinum atoms.

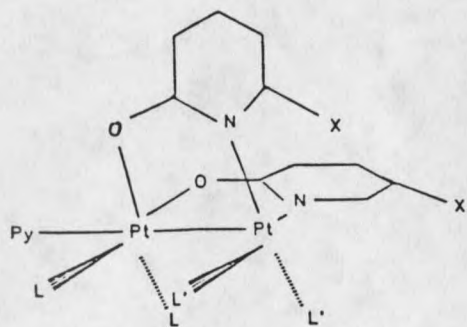
By using a variation of Vrieze's method, Bancroft has synthesized a new class of platinum binuclear compounds which have been confirmed by x-ray crystallography and NMR spectroscopy. This has resulted in interesting geometric and mechanistic insights (52).

This series of the binuclear platinum(III) compounds existed as head-to-head (HH) and head-to-tail (HT) isomers. This HH and HT classification not only depends upon the geometry in which HT has both axial positions occupied while

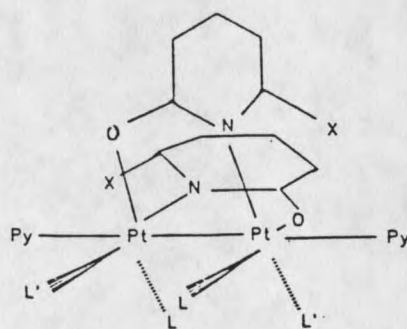
HH has only one axial position occupied and another axial position is available for ligand bonding, but also depends on the size of the substituent on the bridges. If the substituent is large in size like Cl or CH₃, then the complexes form HH or the polar-arrangement. If the substituent is small like H or F, then the complexes can have either polar (HH) or nonpolar (HT) arrangements [17].



Oxopyridonate ligands and their derivatives

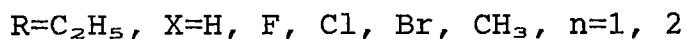
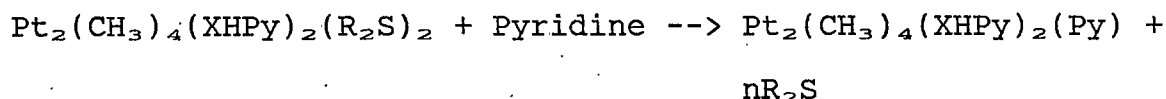
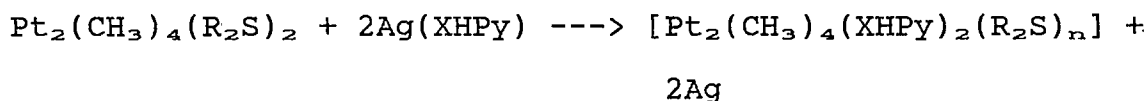
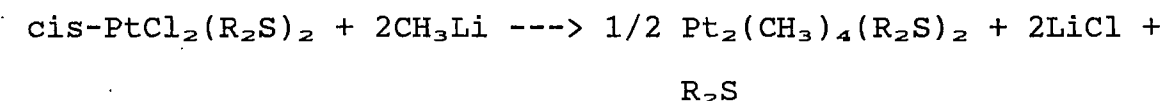
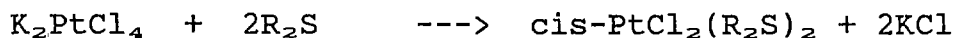


L = L' = CH₃
Head to Head configuration



L = L' = CH₃
Head to tail configuration

The oxopyridonate bridged complexes are prepared by the following reactions:



The platinum(III) complexes are stable in the solid state. NMR studies show that some HH polar complexes are stable in solution while HT complexes are converted to a HT and HH equilibrium mixture in the solution over a period of a few hours.

In summary, much is yet to be learned about platinum cluster chemistry in view of the great structure diversities of the clusters. The objectives of my project were to develop general methods for the synthesis of multinuclear platinum compounds, to characterize the bond formation in these complexes and to investigate the mechanisms of some of the platinum reactions.

The cis-PtCl₂(Et₂S)₂ complex is not considered to be a Pt cluster, but in this special category, I'd rather include

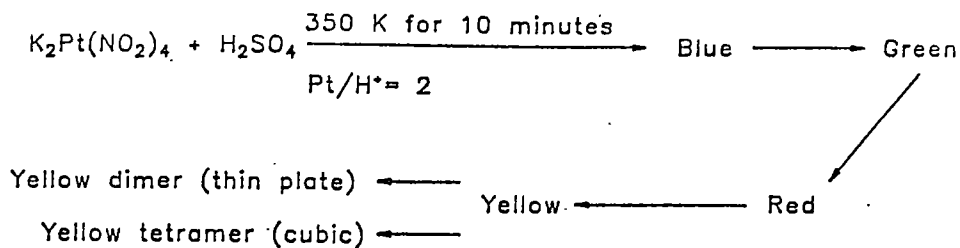
this complex into the consideration due to its importance in the synthesis of the platinum cluster and its functionality in organometallic chemistry. It has been observed that $\text{cis-PtCl}_2(\text{Et}_2\text{S})_2$ isomerizes to $\text{trans-PtCl}_2(\text{Et}_2\text{S})_2$ in solution and $\text{trans-PtCl}_2(\text{Et}_2\text{S})_2$ is the thermodynamically favored product in certain solvents. It is also true that $\text{cis-PtCl}_2(\text{Et}_2\text{S})_2$ is a common starting material for further synthesis because of the labile Pt-Cl bond. A review of the reactions involving related compounds can benefit the understanding of the current investigation.

As my research has been concerned with the formation and breakage of chemical metal-metal bonds, it is important for me to find out and trace reactions involving direct metal-metal bonds or metal atoms bonded by a bridge. There is a interconversion of binuclear platinum(III) complex as I describe earlier in this chapter. Thus, it is my intention to study this interconversion thermokinetically and to learn more detail about this kind of arrangement. The binuclear platinum(III) complex, from the electronic configuration, has a metal-metal bond. Initially, I will attempt to determine whether the metal-metal bond is broken during the $\text{HH} \rightleftharpoons \text{HT}$ interconversion. Then I will examine the rearrangement of the bridge ligands as these ligands in one state "bite" the metal centers and transfer into another state without giving up chelating the metals. Factors affecting this interconversion have been found. Lastly,

theoretical comparison of experimental data brings us to a conclusion that the interconversion happens as a concerted step, neither the metal-metal bond nor the bridging ligand is completely dissociated. Therefore the question of a mixed valence d^6-d^8 (Pt(IV) and Pt(II)) electronic configuration or a d^7-d^7 (Pt(III) and Pt(III)) electronic configuration in the interconversion has been partially clarified as the intact metal-metal bond in the rearrangement. Pt(III) is more reasonable in explaining the metal-metal bond formation. Systematic substitution chemistry of the binuclear Pt(III) compounds reveals the influence of the axial ligand on the metal-metal bond and the torsion angles between the Pt-CH₃ group planes. Different axial ligands result in different torsion angles and bond length changes. The torsion angle is not related to the trans-effect of the axial ligand, it is rather related to the bulk of the axial ligand. The change of the metal-metal bond length seems to be closely related to the trans-effect of the axial ligand.

In the last part of this dissertation, the synthesis and characterization of a group of yellow platinum clusters has been pursued. The synthesis suggested by Blondel (11) by using Pt(IV) oxide reacting with sulfuric acid and oxalic acid has been modified such that a simpler and safer reaction between $Pt(NO_2)_4^{-2}$ and dilute sulfuric acid develops into a new series of platinum complexes. This

reaction is strongly influenced by the pH value of the solution and generates a series of color changes. The synthesis results in a yellow platinum dimer and a yellow platinum tetramer [18].



Synthesis of yellow dimer and tetramer

[18]

While a binuclear platinum(III) sulfato-bridged complex forms in a classic sense of the synthesis (I), compounds characterized by Lippert have similar structures (45). But one should notice the unique aspect of the yellow platinum clusters that nonequivalent oxidation states are found in the platinum tetramer. The research of this particular reaction has given some insights into the formation, structure and reactivity of the platinum cluster. Modern techniques have been used during the investigation. They include nuclear magnetic spectroscopy, single crystal x-ray crystallography, infrared spectroscopy, chromatography and elemental analysis.

My thesis is divided into three parts. Part one deals with cis- and trans-PtCl₂(Et₂S)₂. Their structures were determined by x-ray crystallography and their isomerization reactions were studied. The second part is the kinetic and thermodynamic study on the HH-HT interconversion for Pt(CH₃)₄(C₅H₃FNO)₂(C₅H₅N) by NMR. Part three is the synthesis of a platinum binuclear compound and platinum tetranuclear compound. Structures were characterized by x-ray crystallography, NMR and FTIR. The last part also includes the different substitution reactions for the binuclear platinum(III) compounds. Any implications concerning structure details, thermodynamic results and reaction routes are discussed after each part. General discussion contains the summary of the work and achievement of this investigation.

THE STUDY OF THE CIS TO TRANS ISOMERIZATION
OF DICHLOROBIS(DIETHYLSULFIDE)PLATINUM(II) COMPLEX

Experimental

A. The syntheses of cis-PtCl₂(Et₂S)₂ and trans-PtCl₂(Et₂S)₂

Synthetic methods have been published (53) and compounds were made for the purpose of the investigation.

B. NMR measurements on the equilibrium between cis and trans-PtCl₂(Et₂S)₂

¹H NMR spectra were recorded on a Bruker AC-300 NMR spectrometer. Low temperature experiments were carried out on a Bruker WM-250 spectrometer operating at 250.132 MHz and on a Bruker AM-500 equipped with a variable-temperature probe. Single frequency decoupling experiments were performed and coupling constants were measured. Chemical shifts were referenced to tetramethylsilane.

Equilibrium constants for the cis to trans-PtCl₂(Et₂S)₂ isomerization were determined by ¹H NMR. The measurement of the equilibrium constant for the isomerization was at 298 K. Pure cis-PtCl₂(Et₂S)₂ and trans-PtCl₂(Et₂S)₂ were used as starting materials, respectively. The equilibrium constant was expressed as K, (K= [trans]/[cis]). The concentrations of cis and trans Pt complexes were determined by integration methylene resonances on Et₂S ligands of each complex in NMR spectrum. As the methylene resonances are not well

separated one from another, but are proportional to the concentration, the equilibrium constant was calculated by the formula ($K=[b-a]/[2a]$, $2a=[cis]$, $b=[trans + cis/2]$). Both a and b were methylene proton resonances directly measured from NMR spectrum. The equilibrium mixtures were measured several times over two weeks until calculated constants no longer varied. The value of the equilibrium constant for cis \rightleftharpoons trans-PtCl₂(Et₂S)₂ isomerization in chloroform was 2.2. In comparison, the isomerization went much more quickly in benzene and took only about half as much time as it did in chloroform. The value of the equilibrium constant was 22.40 in benzene.

The kinetics of the cis \rightleftharpoons trans-PtCl₂(Et₂S)₂ isomerization has been previously investigated (54-55). Though the investigation of the cis to trans-PtCl₂(Et₂S)₂ isomerization had been studied for a long time, most of the reports were only concerned with the cis or trans Pt complexes themselves. Because of the instrumentation's limitations, some of the data about the complexes were not well characterized. Recently the study of the cis and trans Pt(II) complexes has shifted to mechanistic research, including oxidation-reduction pathways and synthetic availability of further platinum clusters. Hence, it is useful to summarize this part of the work as a reference to further study.

C. X-ray crystallographic determination of the structure of cis-PtCl₂(Et₂S)₂ and trans-PtCl₂(Et₂S)₂

The synthetic products from the reactions have different colors and crystalline shapes. The crystals of the cis-PtCl₂(Et₂S)₂ complex are greenish yellow and flake-like, while the crystals of the trans-PtCl₂(Et₂S)₂ are orange yellow and tiny needle-like. Both crystals have a metallic shining surface. Single crystals of these two complexes were picked up for x-ray crystallographic determination. Structures for both cis-PtCl₂(Et₂S)₂ and trans-PtCl₂(Et₂S)₂ complexes were solved. They were refined routinely following the standard procedure as described on pages 112 and 114.

Discussion

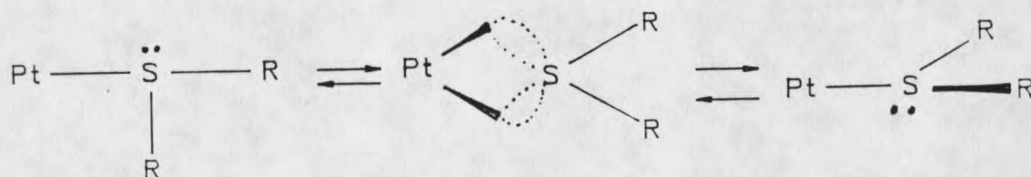
Platinum(II) complexes have been known for many years to have square-planar structures, but it is only in recent years that people began to realize their important role in organometallic and coordination chemistry studies. When we started the Pt cluster research, we found that the cis isomer was a ideal starting material for binuclear Pt(III) complex formation due to the labile metal-ligand interaction. Meanwhile, the cis to trans isomerization was observed and studied by NMR. Therefore, we intended to report the details about the cis and trans isomer structures in this part.

As early as 1888, Blondtrad (56) found that diethylsulfide united with platinum chloride to form a Pt(II) complex with a Pt-S bond. Klason (57) extended this observation and reformulated the structure of the product, in which platinum was quadrivalent. Neither author contemplated a planar configuration or gave satisfactory proof of the structure, although useful and accurate data were accumulated. It was not until Werner (58) attributed the isomerism to the presence of cis and trans-planar forms that it was recognized that platinum exhibited four coordination, as is universally accepted at the present time.

Although many square-planar Pt(II) compounds have been isolated in their cis and trans forms, only a few of them have an observable isomerization in solution. The first study on the cis \rightleftharpoons trans dichlorobis(dialkylsulfide) platinum(II) complexes occurred in 1930 (59) when Angell and Drew observed qualitatively that a cis \rightleftharpoons trans isomerization took place in alcohol. Studies on the thermodynamics of this process were reported in 1952 (60), in which a comparison of equilibrium between cis- and trans-(M Et_3)₂PtCl₂ where M=P, As, Sb. In this paper, the thermodynamic data for the system were collected and the steric effect of the ligands in the cis position was discussed. In 1970, cis-bis(trialkylphosphine)dichloro-platinum(II) was studied kinetically for the cis \rightleftharpoons trans isomerization and the

investigator of this paper postulated that the isomerization took place through the pseudorotation of the phosphine group in a five-coordinate intermediate and the cis ⇌ trans isomerization was catalysed by free phosphine (61).

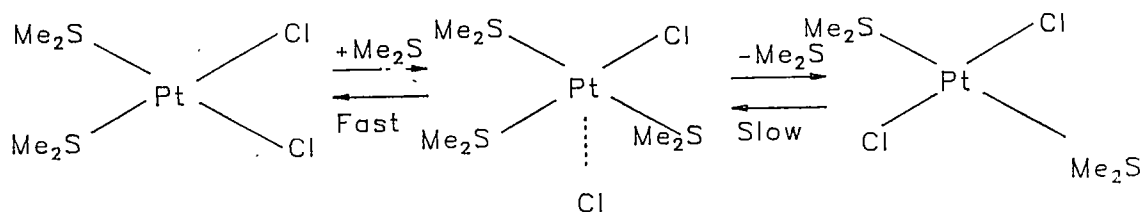
Meanwhile, extensive studies of these platinum-phosphine complexes gave conclusive evidence for the mechanism which required two consecutive steps to effect the cis ⇌ trans isomerization, involving an ionic intermediate and known ligand trans effect. At the early 70's, there was no clear reason for invoking the pseudorotation mechanism for cis ⇌ trans isomerization. Almost at the same time, proton NMR was first used to study the cis ⇌ trans dichlorobis(dialkylsulfide)platinum(II) complexes and the mechanism of the inversion at sulfur was first reported [19](62).



[19]

The observation that the retention of Pt-S-C-H coupling above the coalescence temperature is consistent with the proposal that the inversion process is really an internal displacement of one sulfide electron pair by another sulfide electron pair in a rearrangement mechanism involving pentacoordinate configuration, since bond weakening and bond strengthening are involved. In the isomerization, there is

no sign for the loss of Pt-S-C-H, thus dissociation of the sulfide ligand is impossible. Thus, a reasonable hypothesis is that there is bonding to both sulfur unshared electron pairs so that the platinum atom has a distorted pentacoordinate configuration or an inversion through a partially dissociated state. In this report, the vicinal platinum-proton coupling constants in the cis and trans forms were calculated (62). Several years later, the cis \rightleftharpoons trans bis(dialkylsulfide) dihaloplatinum(II) reaction was studied again using ^1H NMR. Different ΔH , ΔS , ΔG and corresponding equilibrium constants were measured. The mechanism for the cis \rightleftharpoons trans isomerization of bis(dialkylsulfide)-platinum(II) complex was proposed as a double displacement [20] (55).



[20]

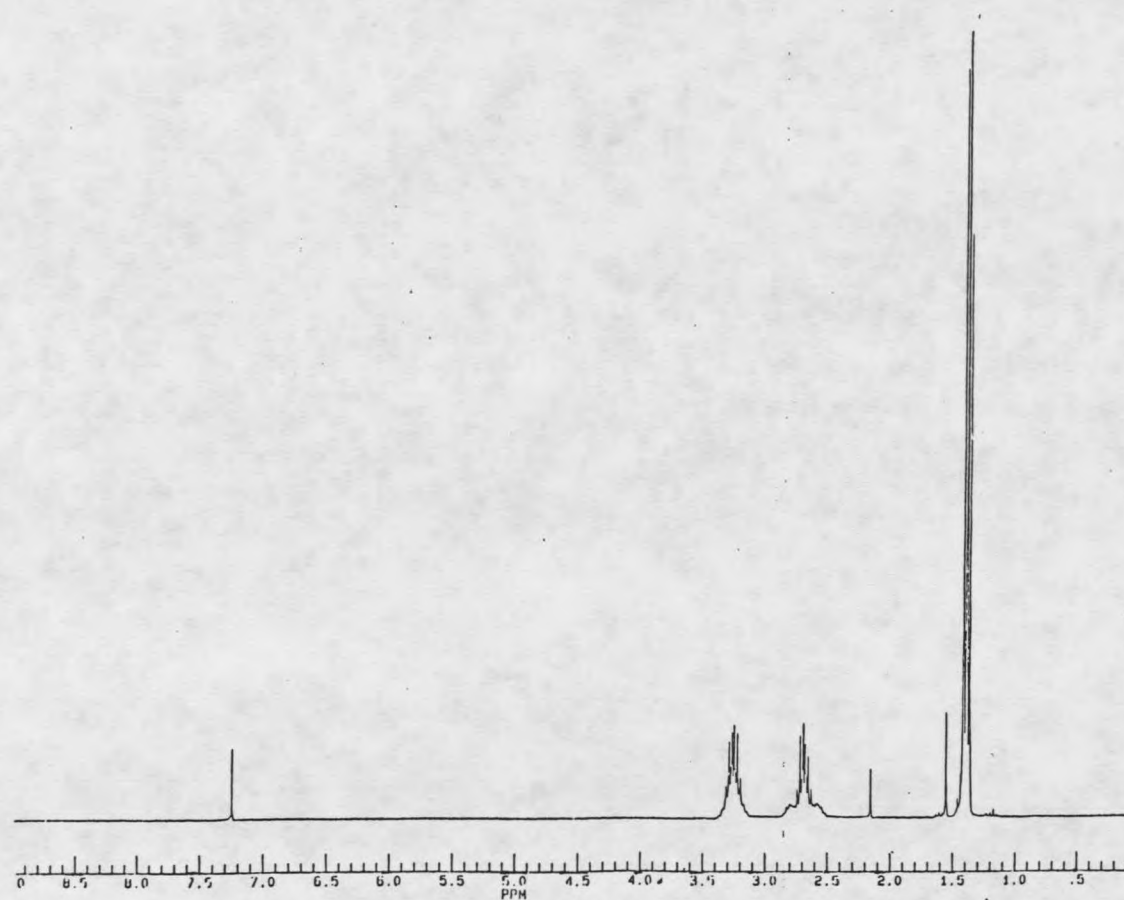
In recent years, study focused on the isomerization has been transferred to cis \rightleftharpoons trans- $\text{PtCl}_2(\text{Et}_2\text{S})_2$ and isomer reactivities; the availability of an oxidative addition pathway has been discovered. Cis- $\text{PtCl}_2(\text{Et}_2\text{S})_2$, with the addition of mesityllithium, produced trans- $\text{PtCl}_2(\text{Mes})(\text{Et}_2\text{S})_2$ (Mes=2, 4, 6 trimethyl phenyl). With the addition of LiBr,

the reaction is accelerated and $\text{Pt}(\text{Br})(\text{Mes})(\text{Et}_2\text{S})_2$ was obtained (63).

The mechanism of the conversion from $\text{cis-PtCl}_2(\text{Et}_2\text{S})_2$ to $\text{trans-PtBr}(\text{Mes})(\text{Et}_2\text{S})_2$ involved the nucleophilic substitution of halide by a mesityl anion and substitution of a chloro ligand by a bromide ligand (63).

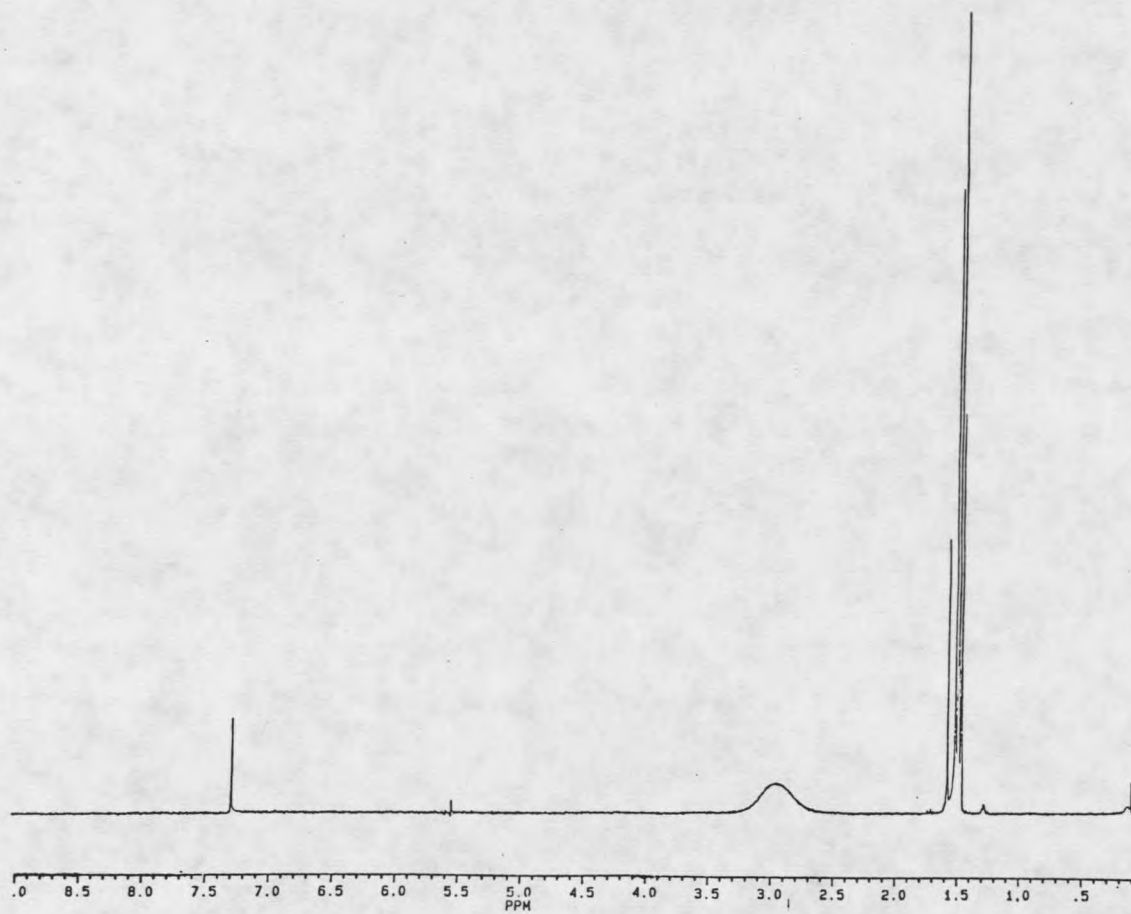
$\text{Trans-PtX}_2\text{L}_2$ ($\text{X}=\text{Cl}, \text{Br}$; $\text{L}=\text{Et}_2\text{S}, \text{Et}_2\text{Se}$) reactions with phenyl, *o*-tolyl were reported in the early 70's (65). As the bonding between a sulfide ligand and $\text{Pt}(\text{II})$ ion is fairly labile, a sulfide group could easily be replaced by other ligands like phosphine, pyridine and carbonyl groups (64). Hence $\text{Pt}(\text{II})$ complex with sulfide ligands is a useful precursor of various organoplatinum complexes. It was also reported that $\text{cis-PtCl}_2(\text{Et}_2\text{S})_2$ is an important starting material for the synthesis of a series of binuclear platinum(III) complexes (52). Earlier work supplied a lot of information about this type of complex, but because of the instruments' limitations (e.g. low sensitivity of NMR and shortage of structure data), there are still quite a few points which have not been explained. It was our goal to collect accurate thermodynamic and kinetic data for the $\text{cis} \rightleftharpoons \text{trans-PtCl}_2(\text{Et}_2\text{S})_2$ process and to structure the complexes in order to improve the synthesis.

^1H NMR data showed (Figures 1-2) that the $\text{cis-PtCl}_2(\text{Et}_2\text{S})_2$ has the two quintet and one triplet resonances in the spectrum due to the sterically nonequivalent



34

Figure 1. ^1H NMR spectrum of $\text{cis-PtCl}_2(\text{Et}_2\text{S})_2$



35

Figure 2. ^1H NMR spectrum of $\text{trans-PtCl}_2(\text{Et}_2\text{S})_2$

methylene protons and equivalent methyl protons of coordinated diethylsulfide. $\text{Trans-PtCl}_2(\text{Et}_2\text{S})_2$ showed a broad unresolved resonance in methylene region at room temperature in the spectrum. This broad resonance was caused by the methylene protons, as methylene groups in $\text{trans-PtCl}_2(\text{Et}_2\text{S})_2$ were fluxional on the NMR time scale. Once the temperature of the experiment was lowered, the fluxionality rate of the $-\text{CH}_2-$, which was either caused by the methylene protons' rotation around S-C1-C2 axis or by the inversion at the sulfur, was slowed down; therefore one could observe the nonequivalent $-\text{CH}_2-$ resonances in the spectrum (Figure 3).

The proton single frequency decoupling experiment not only helps to determine the relation between one proton and another, but it also determines the coupling constant which indicates the interaction between the nuclei. From the decoupling data, we determined that the Pt-H coupling constant is much larger than the H-H coupling, indicating the strong interaction with the heavy atom (Figures 4-5, Table 1). We also notice that coupling constant of cis complex is always larger than that of trans complex. The explanations are based on the coupling through σ and π bond. In this case, the amount of π bond between Pt-S is small. Therefore the larger coupling constant of the cis isomer must have a larger amount of σ bond between Pt-S, so the bond strength between Pt-S increases which also means that

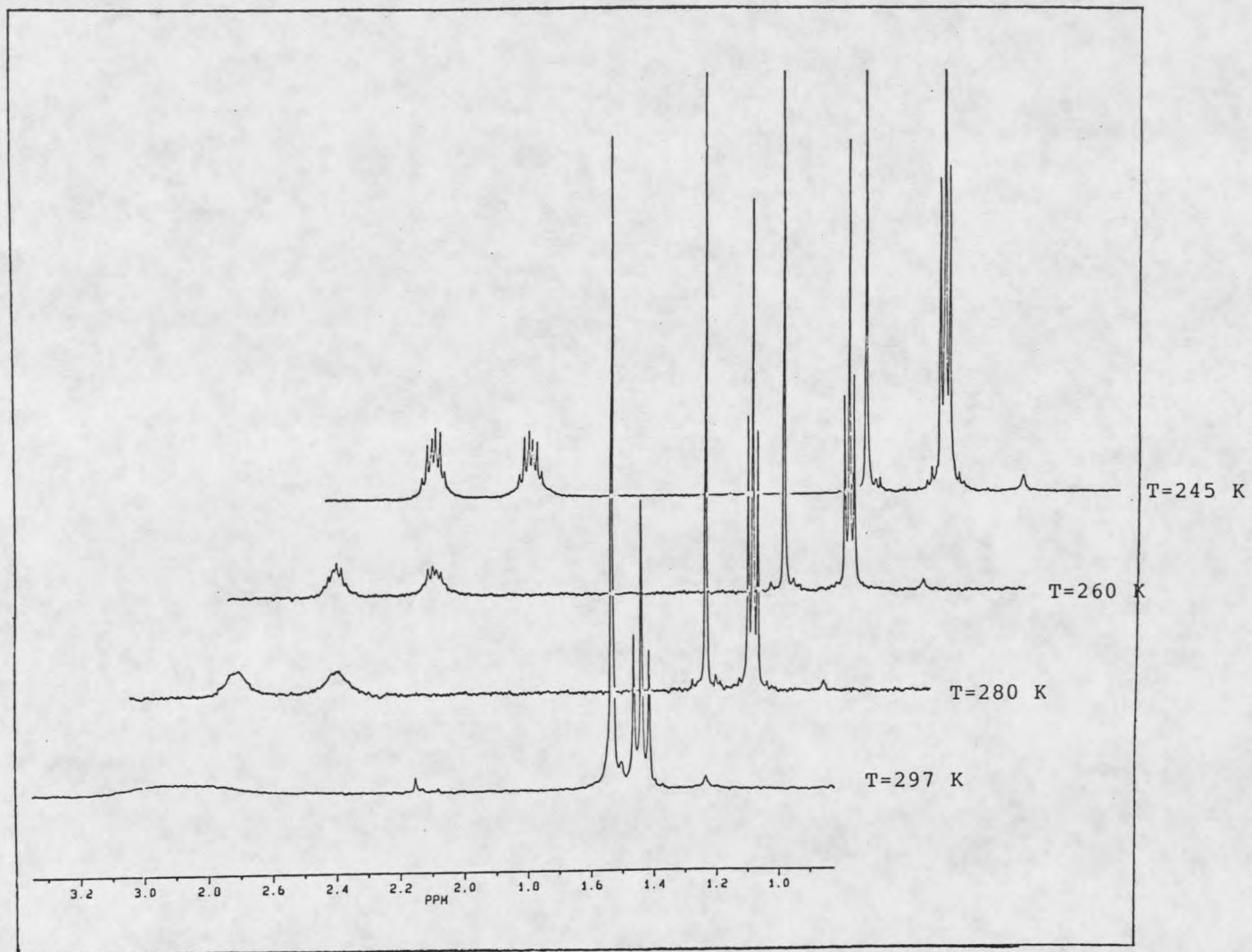


Figure 3. ^1H NMR spectra of $\text{trans-PtCl}_2(\text{Et}_2\text{S})_2$ at different temperatures

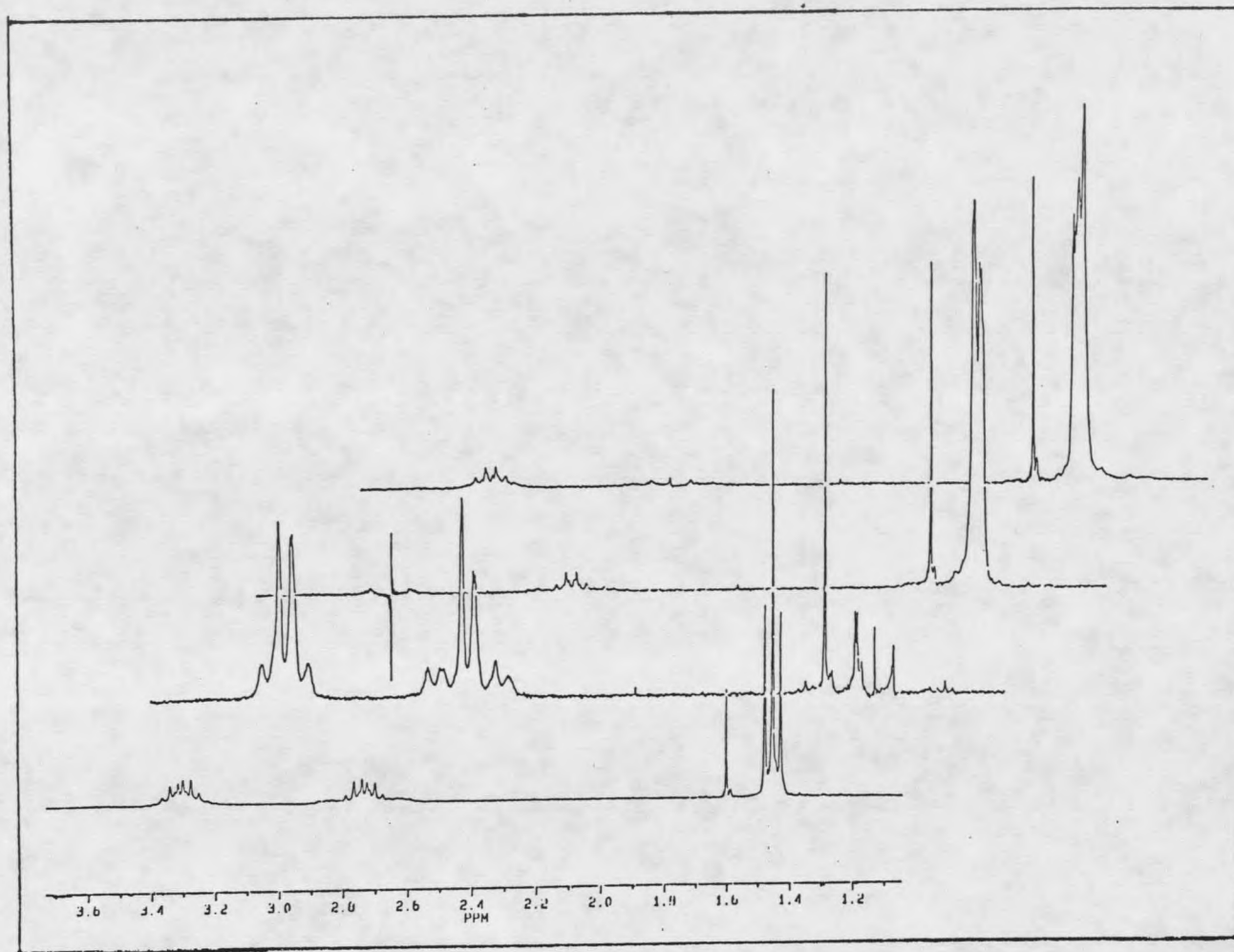


Figure 4. ¹H NMR spectra of decoupling of cis-PtCl₂(Et₂S)₂

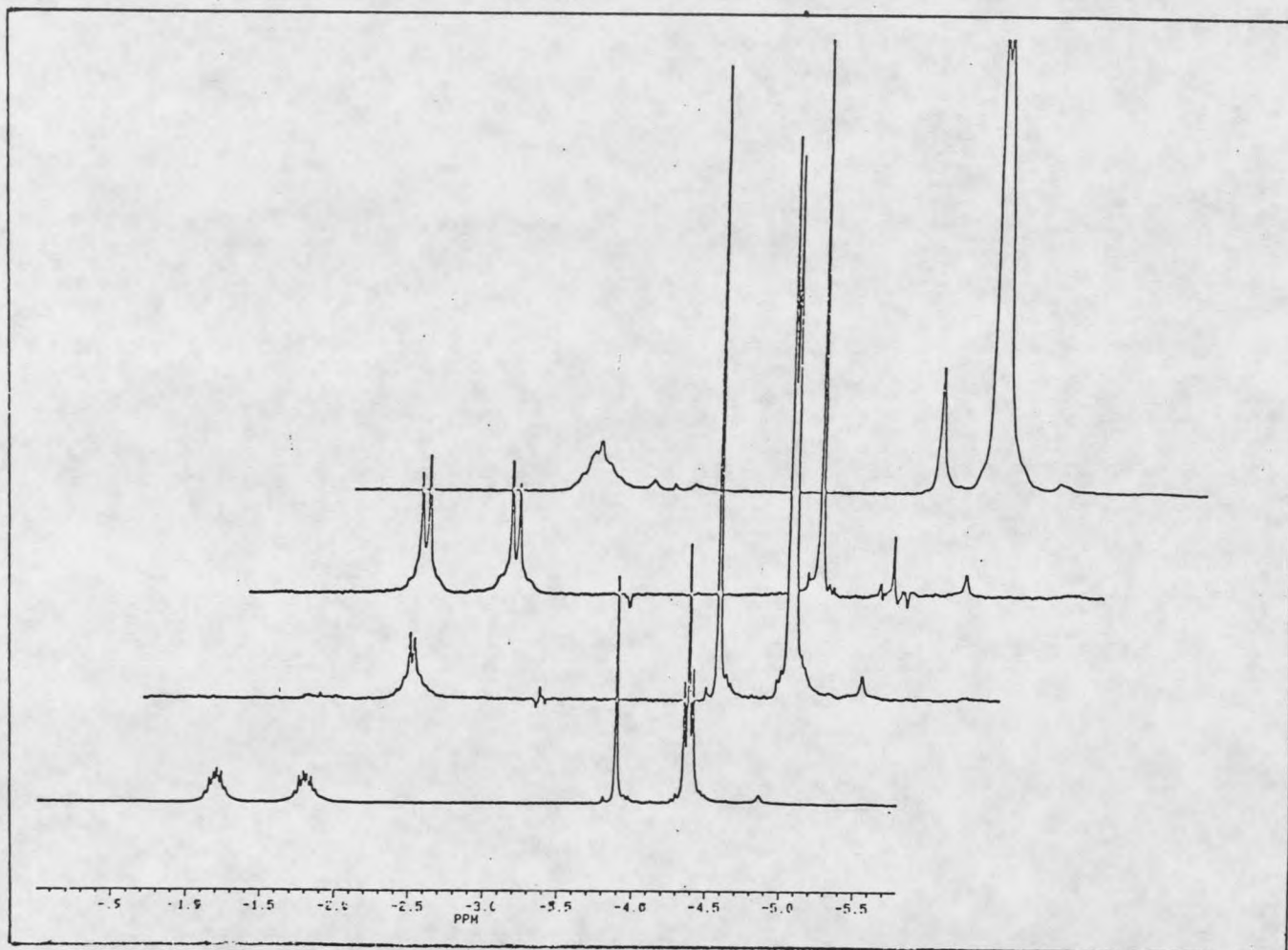


Figure 5. ^1H NMR spectra of decoupling of $\text{trans-PtCl}_2(\text{Et}_2\text{S})_2$

Table 1. Coupling constants for cis-PtCl₂(Et₂S)₂ and trans-PtCl₂(Et₂S)₂

	cis-PtCl ₂ (Et ₂ S) ₂	trans-PtCl ₂ (Et ₂ S) ₂
J _{ab} *	11.4 Hz	7.6 Hz
J(Pt-a)	63.8 Hz	38.8 Hz
J(Pt-b)	34.3 Hz	28.5 Hz
J(a-CH ₃)	9.5 Hz	7.9 Hz
J(b-CH ₃)	6.6 Hz	6.3 Hz

* a and b refer to the methylene protons on Et₂S.

Et₂S is a better ligand in the cis isomer than in trans isomer. The equilibrium constant varies with solvents. Equilibrium constants were measured for CDCl₃ and C₆D₆. Isomerization also occurred in acetone, resulting in a unclear spectrum. Besides cis-PtCl₂(Et₂S)₂ was quite soluble in methanol and quite insoluble in hexane. Those results could indicate that cis-PtCl₂(Et₂S)₂ has considerable polarity.

From the equilibrium constant data, it was concluded that cis ⇌ trans-PtCl₂(Et₂S)₂ isomerization tended to go to less-polar trans-PtCl₂(Et₂S)₂ in less polar media. Because C₆D₆ is less-polar than CDCl₃, the equilibrium constant in C₆D₆ is 10 times larger than that in CDCl₃.

X-ray crystallography was used to characterize cis- and trans-PtCl₂(Et₂S)₂ structures. Both structures show a Pt-S bond length of 2.226-2.301 Å, similar to the Pt-S bond length in Pt(III) complex with Et₂S in an axial position

(2.292-2.303 Å). One might think that the trans- $\text{PtCl}_2(\text{Et}_2\text{S})_2$ should be non-polar due to the symmetry of the complex. But it turns out from structure characterization that since the four $-\text{C}_2\text{H}_5-$ groups lie on the same side of the plane containing platinum, chlorine, and sulfur atoms, the trans complex keeps certain polarity as had been previously determined (2.41 D for trans isomer, 9.5 D for cis isomer (58)).

Finally the rate of cis to trans- $\text{PtCl}_2(\text{Et}_2\text{S})_2$ isomerization, despite the different postulated mechanisms, is directly related to the solvent, because different solvents change the rate of the reaction. The solvent effect on the isomerization is nevertheless related to the ligand substitution. As the enthalpy of the formation of trans- $\text{PtCl}_2(\text{Et}_2\text{S})_2$ is positive ($\Delta H=15$ kcal/mole), thus the cis to trans process is quite endothermic. ΔH for the internal bond strength change and ΔH of solvation are the two major contributions to this enthalpy term. As sulfide ligands have a larger trans-effect than chloro groups, the isomer which allows the greater amount of Pt-sulfur π back donation would have the larger overall bond strength, simply because the isomer with more efficient π bonding would have the greater total bond strength. This is the cis-Pt isomer in which the sulfides ligands are trans to the chloro ligands. As for the ΔH of solvation, the dipole-dipole interaction between the complex and the solvent are greater

in the more polar cis-Pt complex than in the less-polar trans-Pt isomer (55).

For the entropy of the process, obtaining a positive ΔS (3 eu) would favor the trans-Pt(II) complex, since the cis-Pt(II) complex would have more associated solvent molecules than the less-polar trans Pt complex due to the stronger interaction between cis-PtCl₂(Et₂S)₂ and the solvent. The rate determining step of the isomerization has been claimed to be the formation by a slow substitution of one chloride by a sulfide, followed by the fast substitution of one of the two sulfides trans to each other by a chloride (55).

It is up to this point that cis \rightleftharpoons trans-PtCl₂(Et₂S)₂ isomerization has been studied.

THE THERMODYNAMIC AND KINETIC STUDIES
ON SOME OF THE BINUCLEAR PLATINUM(III) COMPOUNDS

Experimental

A. Syntheses of the binuclear Pt(III) compounds

The preparation of a series of platinum(III) complexes for the purpose of this investigation has been described (52). These binuclear Pt(III) compounds include Pt(HPy) (HH and HT), Pt(FHPy) (HH and HT), Pt(CHPy) (HH) and Pt(MHPy) (HH).

B. NMR measurements

The NMR assignments on these binuclear Pt(III) compounds were carried out with a Bruker WM-250 operating at 250.132 MHz for proton spectroscopy, 62.80 MHz for carbon-13 and 53.518 MHz for platinum-195. Chemical shifts are referred to tetramethylsilane for proton and carbon-13 spectra. For platinum-195, the standard is 1 M H_2PtCl_6 . Nuclear Overhauser enhancements were measured by the difference method. All solvents were bought from Aldrich and used without further purification.

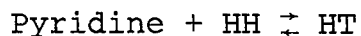
C. NMR spectral assignments for a series of Pt(III) compounds

The molecular structures of the series of binuclear Pt(III) compounds have been elucidated (52). There are two kinds of structures for some of the Pt(III) compounds, one

is known as head to head (HH) or the polar Pt(III) complex, another is known as head to tail (HT) or the non-polar Pt(III) complex. The differences between HH and HT are whether the axial positions are occupied by one ligand or two ligands and the coordination around each Pt as described on page 21. There is an interconversion between HH and HT when addition or removal of axial ligands happens. The proton NMR assignments for these Pt(III) compounds are listed in Tables 2-7 and the NMR spectra are shown in Figures 6-11. Protons on the hydroxypyridine ligands were readily assigned by comparison of the unsubstituted complex with the 6-substituted complexes. The 5-H on the hydroxypyridine ligand is a multiplet in the former case but is a doublet in the latter case. The 3 and 4-H's are the remaining doublet and triplet, respectively. Single frequency decoupling and a COSY experiment confirmed these assignments.

D. Equilibrium constant measurement on the HH \rightleftharpoons HT interconversion

The equilibrium constant for the HH \rightleftharpoons HT binuclear Pt(III) compounds interconversion has been determined by proton NMR. The equilibrium between HH to HT is expressed as:



The equilibrium constant is $K = [\text{HT}] / \{[\text{HH}] \times [\text{Py}]\}$. The measurement starts with the addition of free pyridine to the

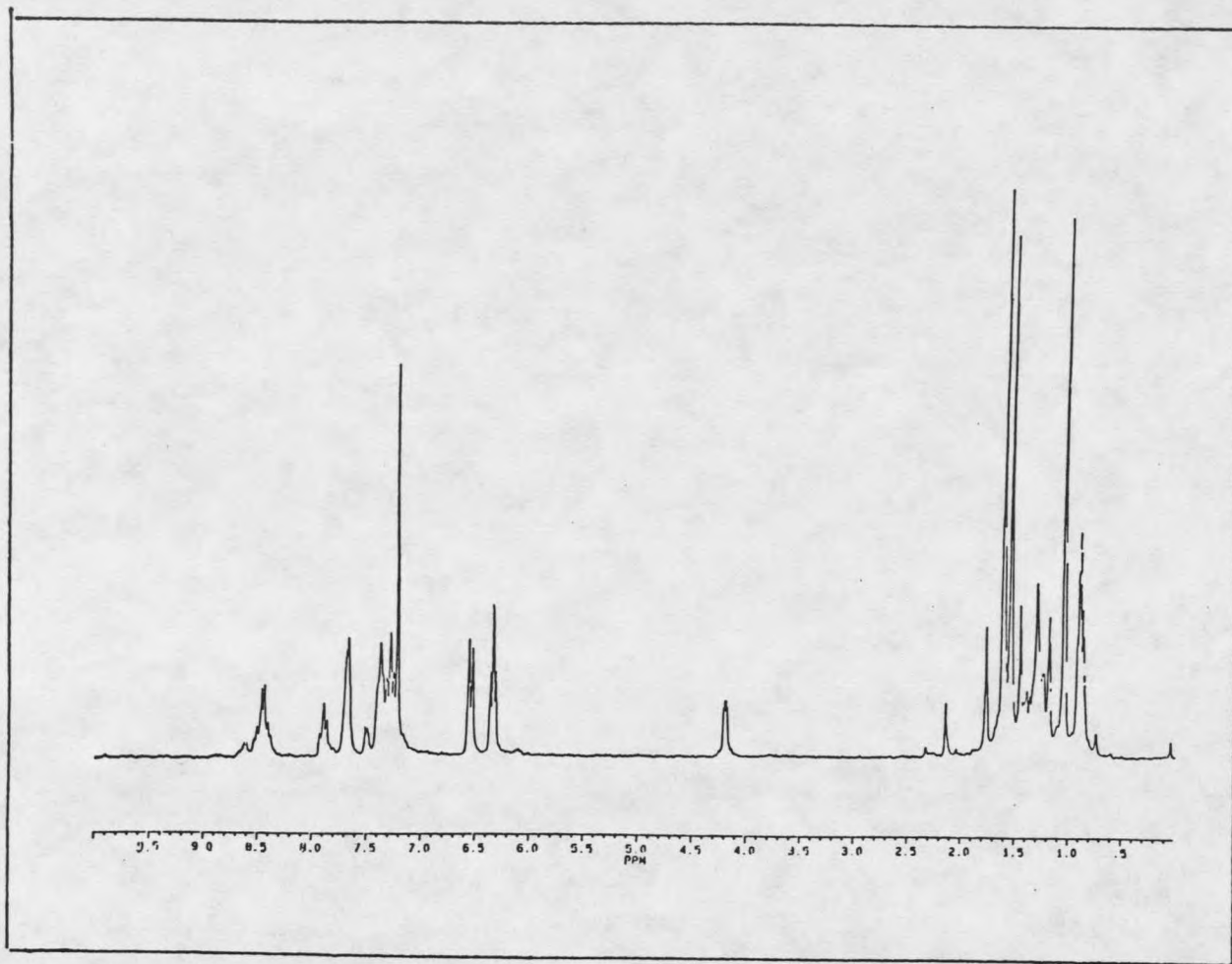


Figure 6. ¹H NMR spectrum of Pt₂(CH₃)₄(HP)₂(Py)

Table 2. ^1H NMR assignments for $\text{Pt}_2(\text{CH}_3)_4(\text{HPy})_2(\text{Py})$

Chemical shift (ppm)	Assignment	Coupling constant ($^2\text{J Pt-CH}_3$)
1.05	$\text{CH}_3(\text{I})$	72.1 Hz
1.62	$\text{CH}_3(\text{II})$	80.5 Hz
6.35	5-H	
6.56	3-H	
7.30	4-H	
7.40	6-H	
7.24	CDCl_3	
7.70	β H-pyridine	
7.92	γ H-pyridine	
8.47	α H-pyridine	

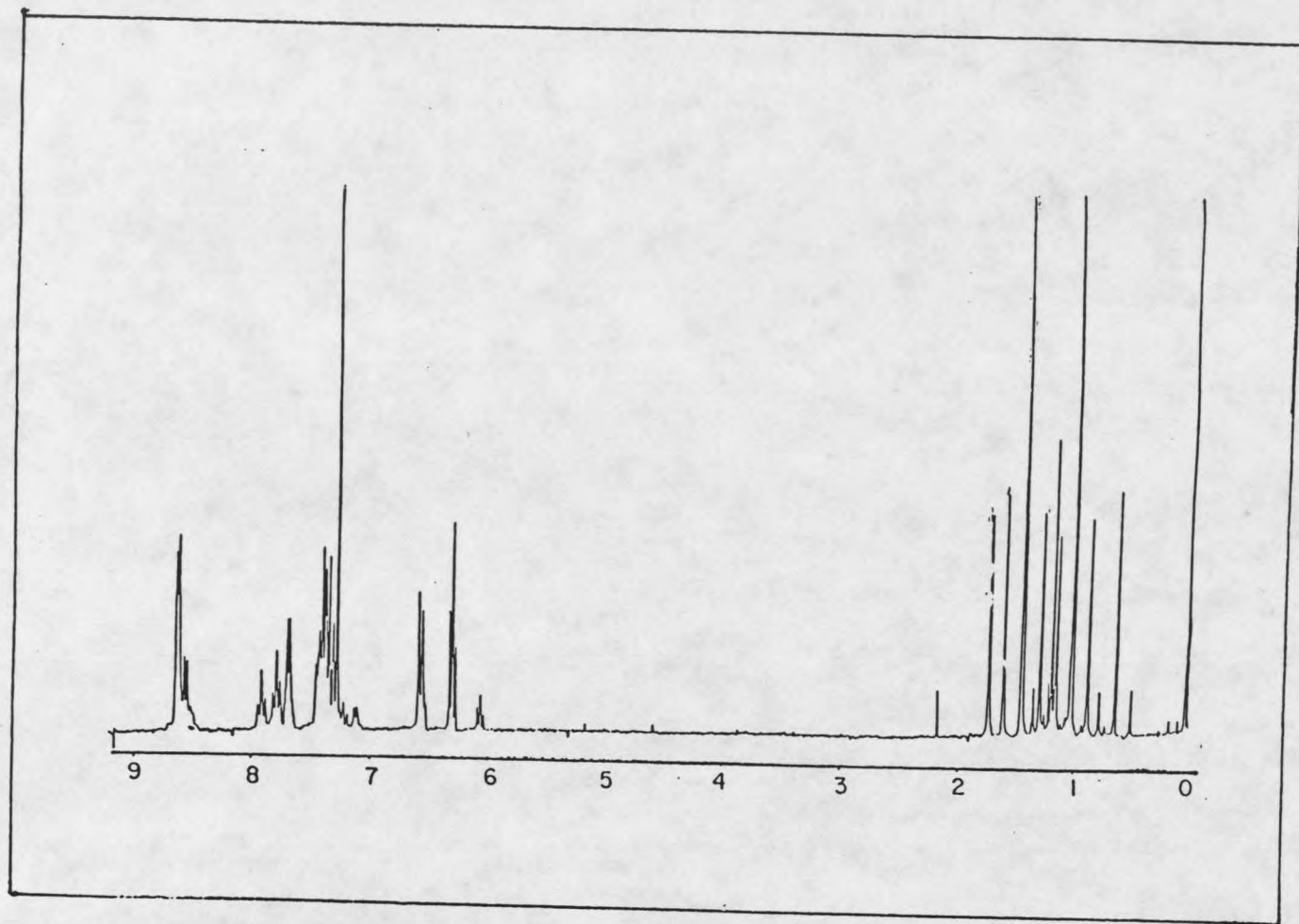


Figure 7. ^1H NMR spectrum of $\text{Pt}_2(\text{CH}_3)_4(\text{HP})_2(\text{Py})_2$

Table 3. ^1H NMR assignments for $\text{Pt}_2(\text{CH}_3)_4(\text{HPy})_2(\text{Py})_2$

Chemical shift (ppm)	Assignment	Coupling constant (^2J Pt- CH_3)
0.64	CH_3 (I)	69.9 Hz
1.16	CH_3 (II)	78.7 Hz
5.72	5-H	
7.22	4-H	
7.36	3-H	
7.24	CDCl_3	
7.40	β H-pyridine	
7.85	γ H-pyridine	
8.70	α H-pyridine	

* Note 6-H not observed

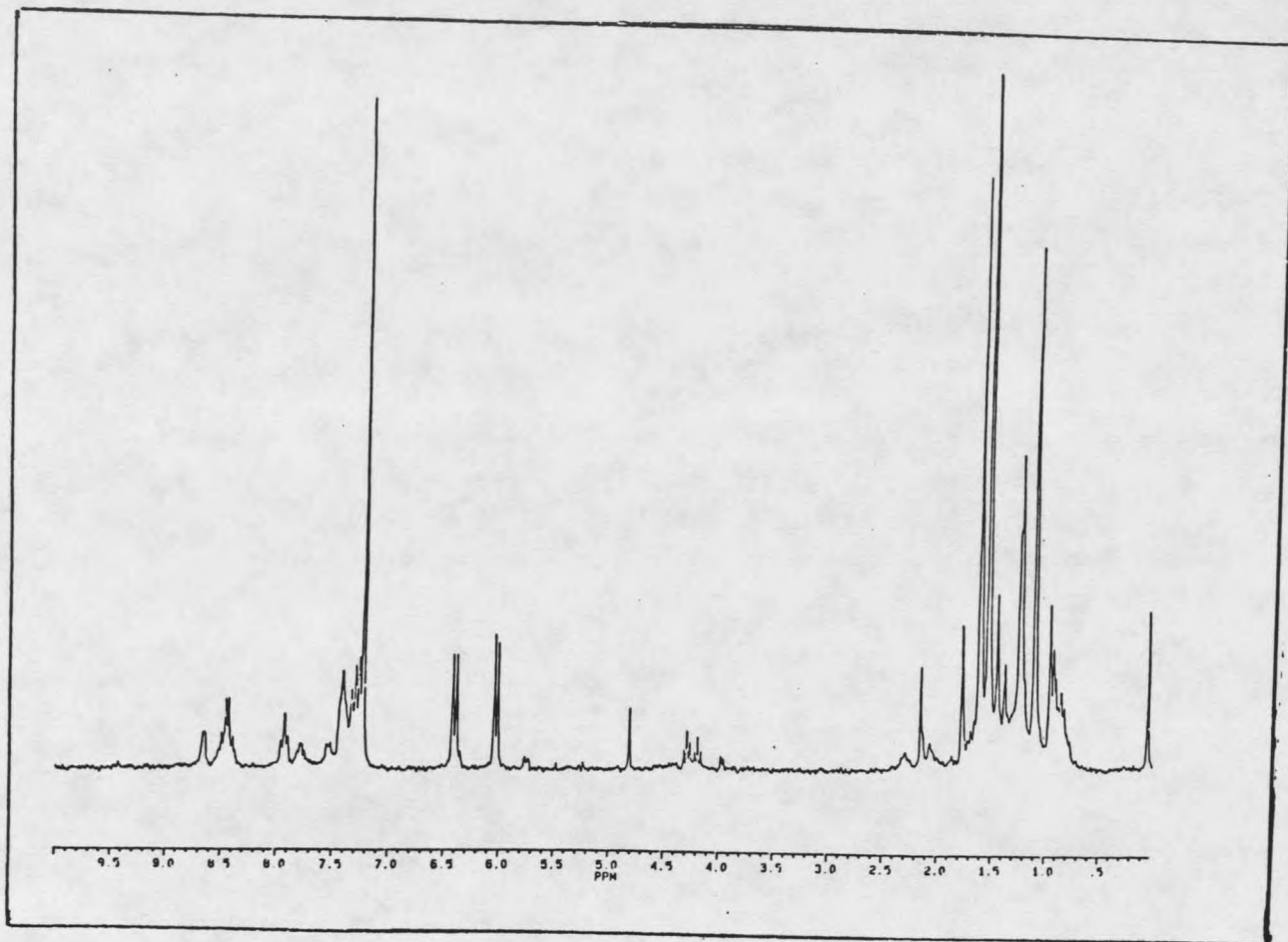


Figure 8. ^1H NMR spectrum of $\text{Pt}_2(\text{CH}_3)_4(\text{FHP})_2(\text{Py})$

Table 4. ^1H NMR assignments for $\text{Pt}_2(\text{CH}_3)_4(\text{FHPy})_2(\text{Py})$

Chemical shift (ppm)	assignment	Coupling constant (2J Pt- CH_3)
1.11	$\text{CH}_3(\text{I})$	69.8 Hz
1.77	$\text{CH}_3(\text{II})$	79.3 Hz
6.07	5-H	
6.43	3-H	
7.26	4-H	
7.24	CDCl_3	
7.30	β H-pyridine	
7.80	γ H-pyridine	
8.46	α H-pyridine	

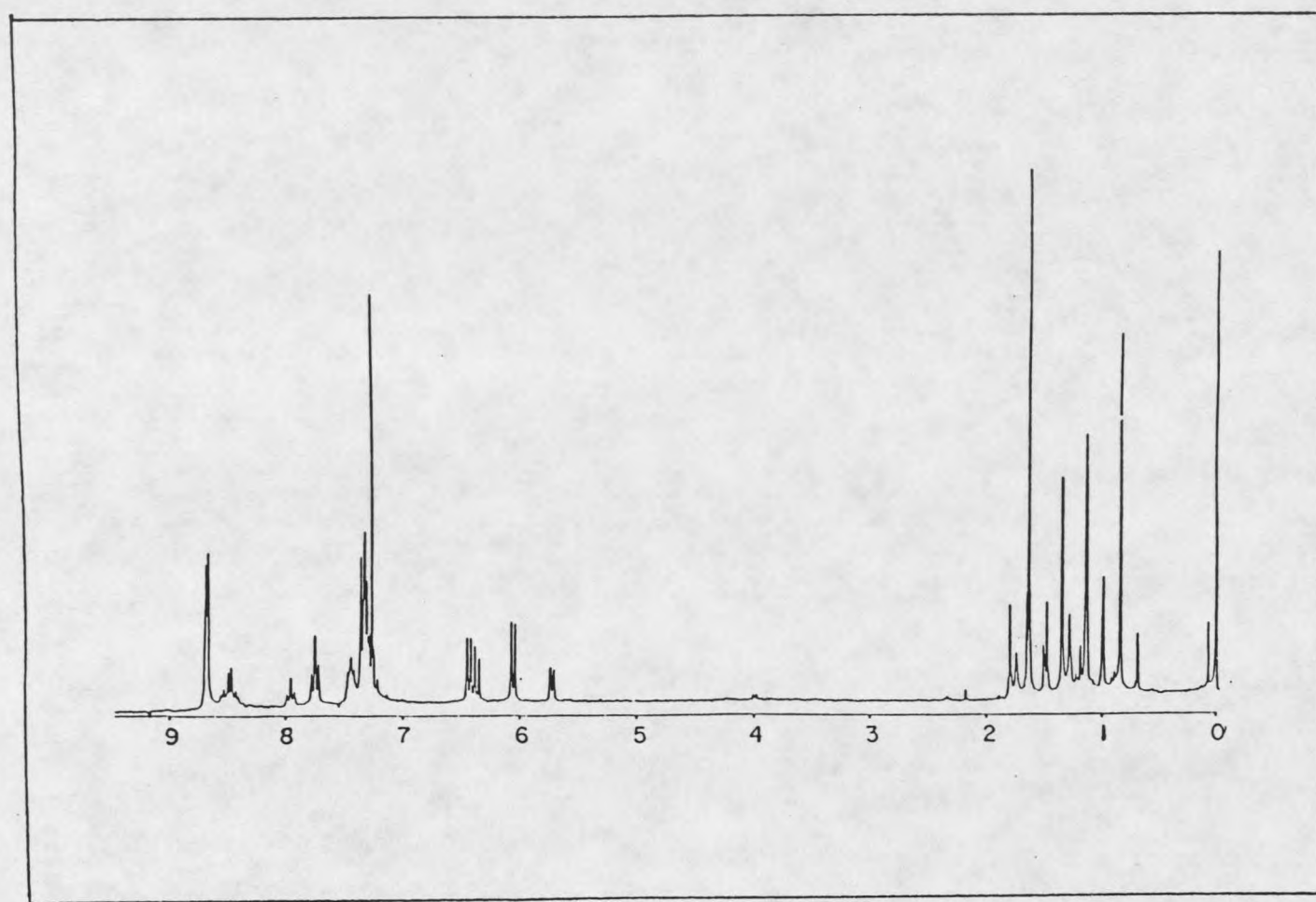


Figure 9. ¹H NMR spectrum of Pt₂(CH₃)₄(FHP)₂(Py)₂

Table 5. ^1H NMR assignments for $\text{Pt}_2(\text{CH}_3)_4(\text{FHP}_\gamma)_2(\text{Py})_2$

Chemical shift (ppm)	Assignment	Coupling constant (^2J Pt- CH_3)
1.13	CH_3 (I)	80.5 Hz
1.61	CH_3 (II)	72.6 Hz
5.69		
5.73	5-H	
6.34		
6.38	3-H	
7.30	4-H	
7.24	CDCl_3	
7.45	β H-pyridine	
7.74	γ H-pyridine	
8.52	α H-pyridine	

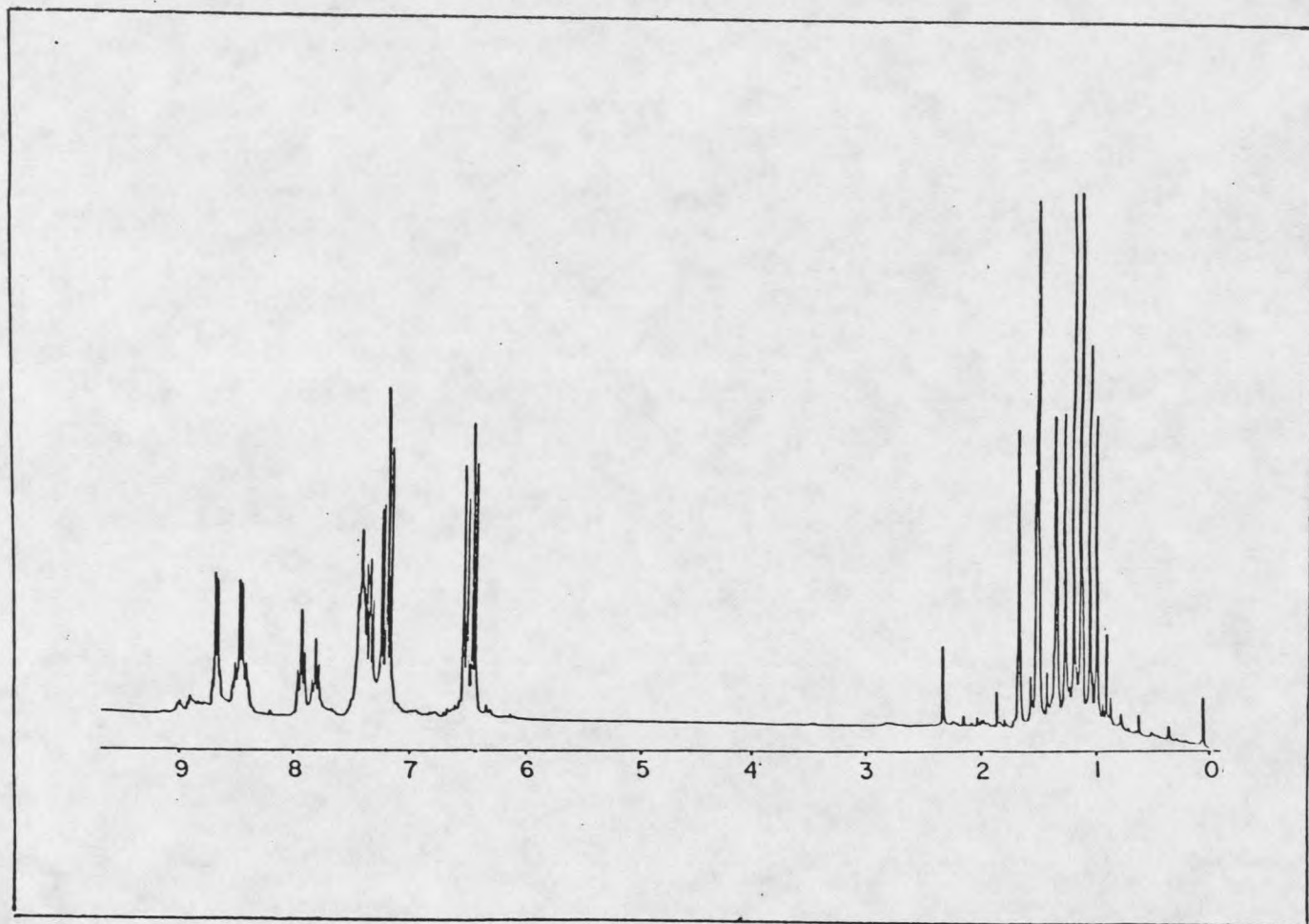


Figure 10. ^1H NMR spectrum of $\text{Pt}_2(\text{CH}_3)_4(\text{CHPy})_2(\text{Py})$

Table 6. ^1H NMR assignment for $\text{Pt}_2(\text{CH}_3)_4(\text{ClHPy})_2(\text{Py})$

Chemical shift (ppm)	Assignment	Coupling constant (^2J Pt- CH_3)
1.15	CH_3 (I)	70.2 Hz
1.46	CH_3 (II)	79.6 Hz
6.40	5-H	
6.45	3-H	
7.14	4-H	
7.24	CDCl_3	
7.36	β H-pyridine	
7.88	γ H-pyridine	
8.40	α H-pyridine	

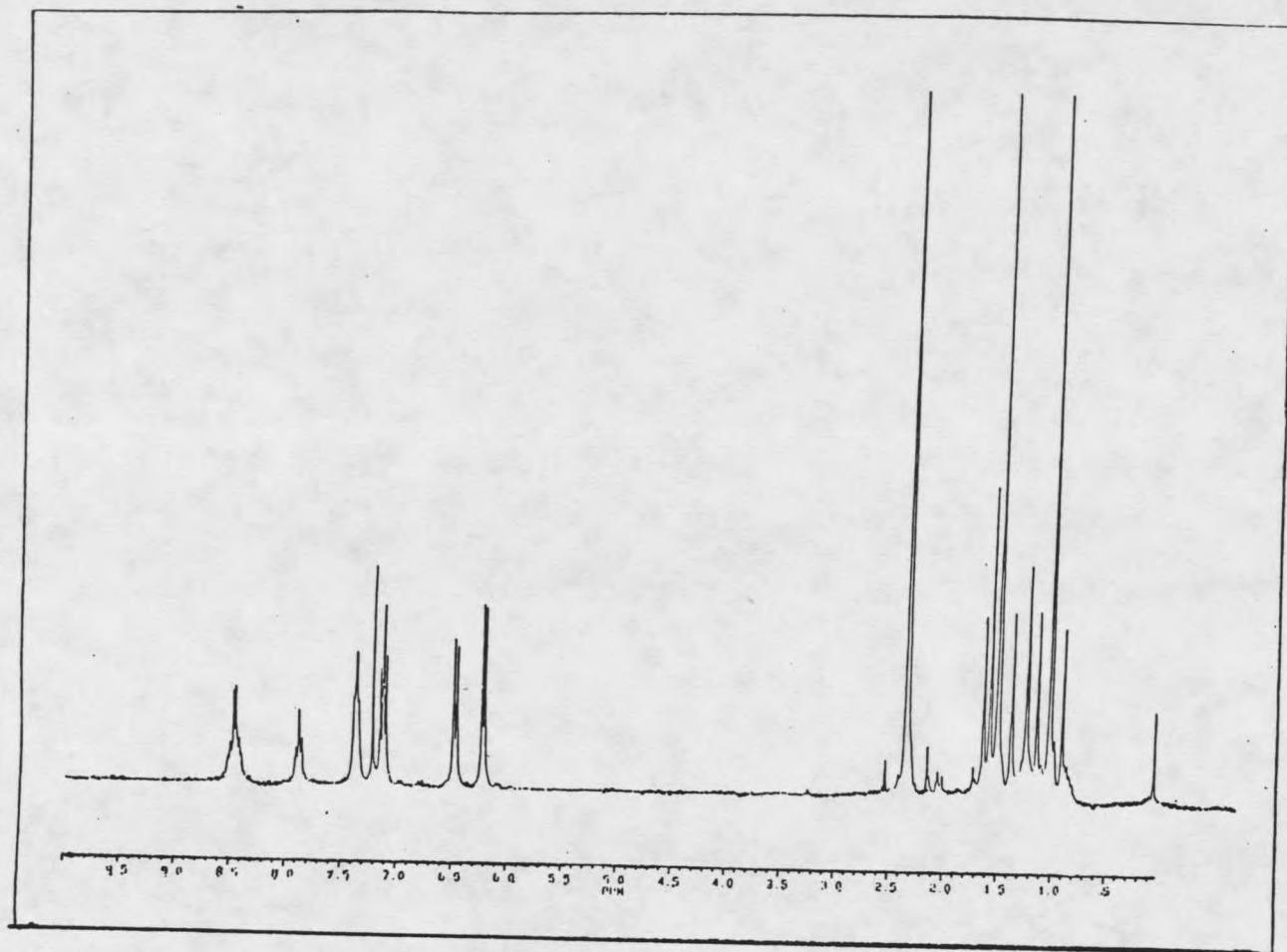


Figure 11. ¹H NMR spectrum of Pt₂(CH₃)₄(MHPy)₂(Py)

Table 7. ^1H NMR assignments for $\text{Pt}_2(\text{CH}_3)_4(\text{MHPy})_2(\text{Py})$

Chemical shift(ppm)	Assignment	Coupling constant (^2J Pt- CH_3)
1.03	CH_3 (I)	69.8 Hz
1.50	CH_3 (II)	79.3 Hz
2.36	CH_3 on the ring	
6.23		
6.25	5-H	
6.48		
6.52	3-H	
7.15	4-H	
7.24	CDCl_3	
7.39	β H-pyridine	
7.91	γ H-pyridine	
8.49	α H-pyridine	

Pt(III) compound (HH), or through dissociation of pure HT isomers into equilibrium mixtures of HH complex and free pyridine. The HT complex is in fast exchange with free pyridine while the HH complex is in slow exchange with the pyridine, leading to different pyridine resonances in the NMR spectra.

Integration of the α proton resonance on the axial coordinated pyridine gives the measure of ratio of HH complex to the HT complex plus the free pyridine. The 5-H proton resonance on the oxo-pyridonate bridge of the HH complex is well separated from the one of the HT, so integration of that region gives the ratio of the HH to HT. An understanding of the total Pt(III) complex concentration makes it possible to calculate all relevant concentrations from these equations:

$$[\text{HH}] / [\text{HT}] = \text{ratio}$$

$$[\text{HH}] + [\text{HT}] = \text{known concentration}$$

The interconversion between HH \rightleftharpoons HT reaches equilibrium slowly, hence the Pt(III) sample was kept in a water bath at constant temperature and measured periodically. The equilibrium constant was measured at different pyridine concentrations and at different temperatures. The data, (Table 8), indicated the interconversion between HH \rightleftharpoons HT thermodynamically favors the HT state. Equilibrium constants and thermodynamic parameters for Pt(FHPy) are tabulated in Table 8. Spectra are shown in Figures 12-13.

The size of the substituent on the oxopyridonate bridge determines whether the HH \rightleftharpoons HT interconversion happens or not. Addition of pyridine to the Pt(HPy) and Pt(FHPy) (both are HH) complexes resulted in the progressive conversion to the HT isomer. Addition of free pyridine to the Pt(MHPy) (HH) and Pt(ClHPy) (HH) resulted in no detectable formation of the HT Pt(III) complex even after several months. Comparison of the size of the substituents on bridging ligand from x-ray crystallographic data indicates that pyridine can interact sterically with the substituent. Larger substituents are able to block the portion that pyridine uses to coordinate with the platinum ion, while smaller substituents do not hinder this pathway for bonding.

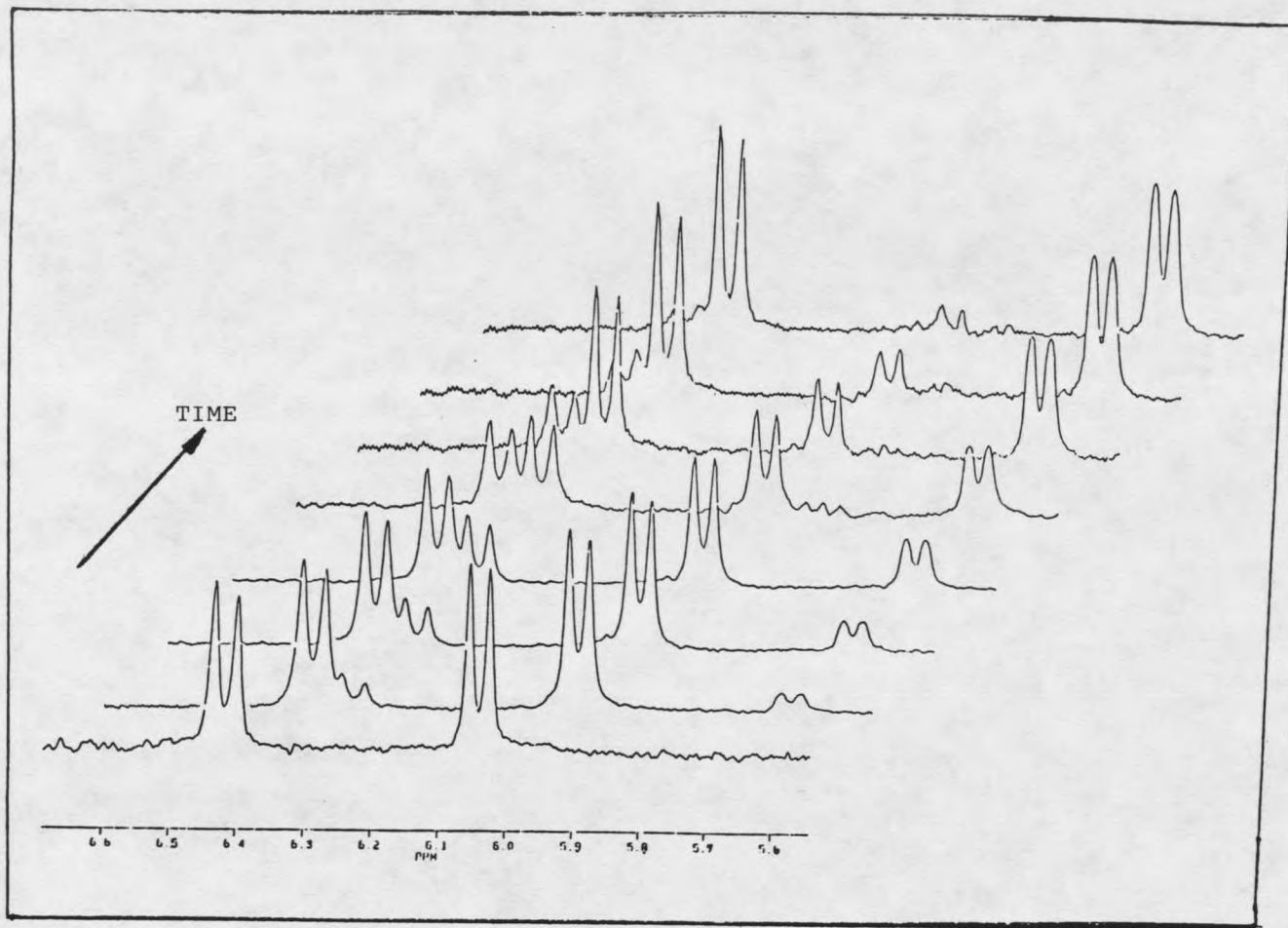


Figure 12. ^1H NMR spectrum of $\text{Pt}(\text{FHPy})$ $\text{HH} \rightarrow \text{HT}$

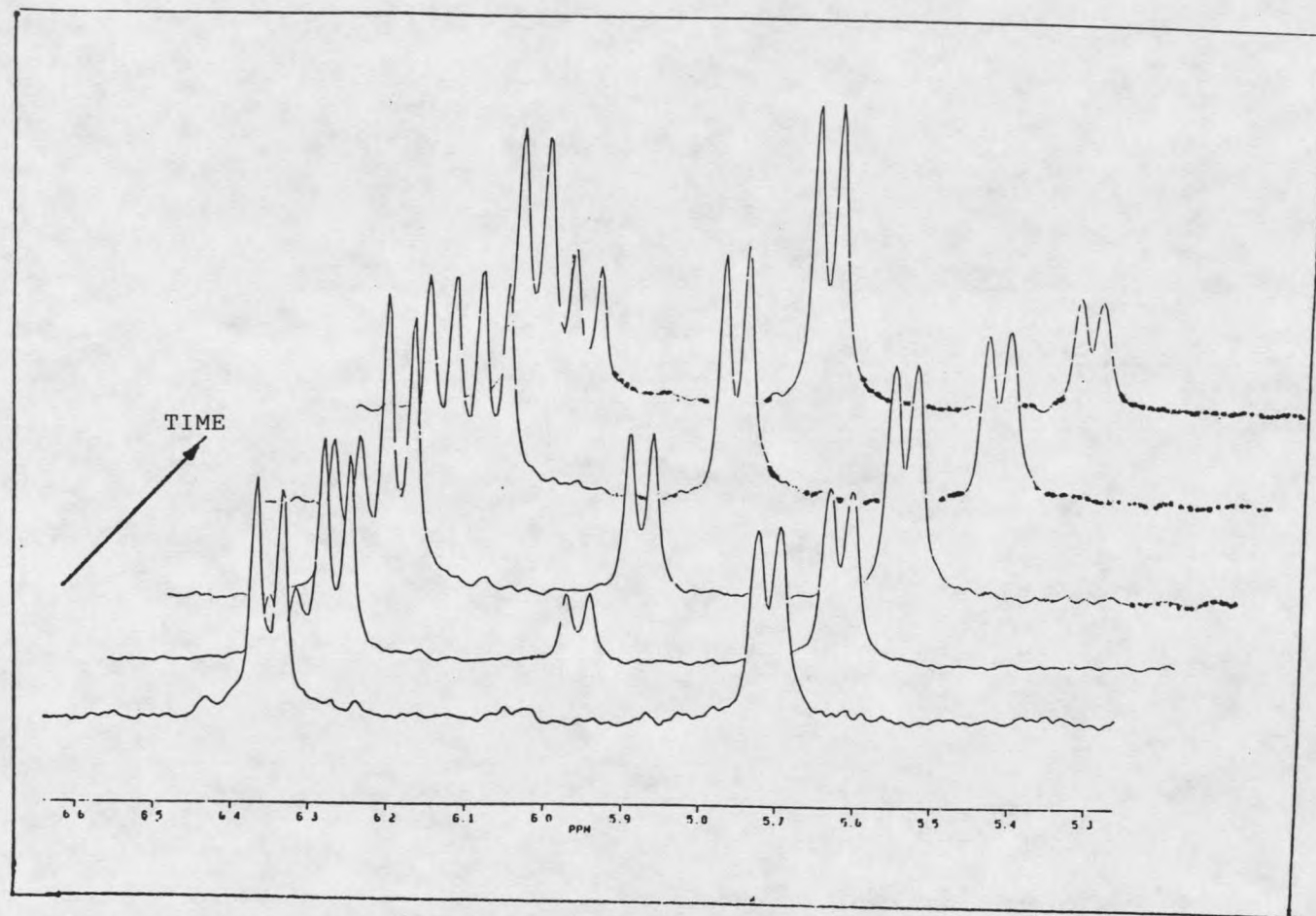


Figure 13. ^1H NMR spectrum of $\text{Pt}(\text{HPy})$ $\text{HH} \rightarrow \text{HT}$

Table 8. Equilibrium constant and thermodynamic parameters for Pt(FHPy) HH \rightleftharpoons HT

^a Equilibrium constant K (M ⁻¹)		[P _y] (M)
26		0.173
24		0.320
21		0.375
27		0.468

K (M ⁻¹)	^b ΔG° (kJ./Mol)	Temperature (K)
26	-8.0	296
20	-7.6	307
15	-7.2	318

ΔS° = -38 J./(K. Mol.)	ΔH° = -19 kJ./Mol.
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a. Temperature = 298 K; standard deviation is ±2.

b. ΔG° = -RTln(K)

E. Kinetic study of the binuclear Pt(FHPy) HH \rightleftharpoons HT interconversion

The kinetic study on the HH \rightleftharpoons HT interconversion for Pt(FHPy) was conducted by proton NMR spectroscopy. The sample of Pt(FHPy) (HH) was kept in a constant temperature water bath and different concentrations of pyridine added into the sample dissolved in CDCl₃. Rate constants were derived and calculated based on the integration ratio of the HH/HT resonance from NMR measurements. The temperature dependence of this interconversion was also determined. ΔS°

and ΔH^\ddagger values of the reaction were calculated based on the microscopic reversibility principle and Eyring plot (Table 9).

Discussion

Tables 1-6 present the chemical shift and coupling constant data for these binuclear Pt(III) series complexes. Protons on the oxopyridonate ligand are readily assigned by the comparison of the unsubstituted hydroxypyridine with the 6-substituted F, Cl or CH₃ group complex, the nearby 5-H proton is a triplet in the former case where it is a doublet in the substituted F, Cl or CH₃ group case. The 3-H and 4-H are assigned by the single frequency decoupling and remained as a doublet and triplet in the ¹H NMR spectra in either case.

The methyl resonances of the complexes are easily assigned by the interaction with the platinum ion which has 30% spin 1/2 nucleus, forming an apparent triplet. This triplet resonance results from the magnetic field caused by the 1/2 spin of platinum nucleus. If the magnetic field is along the direction of the external magnetic field, the nuclear magnetic momentum of the proton nucleus would be enhanced, so the chemical shift of the proton would go downfield. If, however, the magnetic field of the nucleus spin is against the direction of the external field, the nuclear magnetic momentum of the proton would be decreased,

and the chemical shift of the proton would go upfield. The center of the apparent triplet is due to methyl groups on Pt with no spin. The triplet 1:4.67:1 ratio is due to the 30% of platinum nuclear spin. A measurement of the distance between the outer wings of the triplet would determine the Pt-CH₃ coupling constant.

In the HH case, two chemically equivalent methyl groups are on each Pt ion while each Pt ion has two different methyl groups on it in the HT case [17]. This is due to the CH₃ group trans to nitrogen and oxygen atom on the oxopyridonate ligands in HT form or cis to these atoms in HH case. The chemical shifts for the methyl group in HH and HT cases have been measured. If a HT arrangement with a single axial ligand existed, the methyl resonances would be different from those observed in the di-axial substituted case in that one ought to see four different methyl resonances. This is not the situation encountered in the measurement.

Nuclear Overhauser enhancement serves to identify the methyl groups in the HH and HT cases respectively if the axial ligand is pyridine. In the HH case, irradiation of the downfield methyl resonance results in the enhancement of the α proton resonance on the axial pyridine (α , β , γ refer the resonances on Py), while the upfield methyl resonance shows no interaction with the proton resonance on pyridine proving that a downfield methyl resonance is closer to the

coordinated pyridine. In the HT case, irradiation of each of the methyl resonances separately results in the same enhancement of the α proton on the axial pyridine, supporting the diaxial substituted structure.

Carbon-13 and platinum-195 NMR assignment for these binuclear Pt(III) compounds were previously described (18), giving a fully-described structure of these Pt(III) complexes.

For the equilibrium $\text{HH} + \text{free pyridine} \rightleftharpoons \text{HT}$, the variation of the pyridine concentration is shown in Table 9. The equilibrium constant obtained by the method described in the experimental section for Pt(HPy) and Pt(FHPy) is thermodynamically reasonable, in which K for Pt(HPy) is about 150 LMol^{-1} and for Pt(FHPy) is about 25 LMol^{-1} at room temperature in CDCl_3 , meaning there is more HT formation in Pt(HPy) compared with HT formed in the Pt(FHPy) at the same pyridine concentration. The reason for the difference in the equilibrium constant for Pt(HPy) and Pt(FHPy) might be due to steric bulk of the substituent on Pt(FHPy). Pt(HPy) is less hindered. It is Pt(HPy) that is more likely to accept the coordinating axial pyridine and transforms to HT form. The failure of Pt(MHPy) and Pt(ClHPy) to form HT complexes is attributed to the steric bulk of the 6-X substituent as well. Therefore, the value of K is directly related to the substituent.

Table 9. Rate constant and activation parameters for Pt(FHPy) HH \rightleftharpoons HT reaction

^a Rate constant (s ⁻¹)	Pyridine concentration (M)	
7.94 x 10 ⁻⁵	0.173	
1.96 x 10 ⁻⁴	0.320	
2.30 x 10 ⁻⁴	0.375	
3.64 x 10 ⁻⁴	0.468	

^b Rate constant(s ⁻¹)	Temperature (K)	
7.94 x 10 ⁻⁵	296	
3.18 x 10 ⁻⁴	307	
7.36 x 10 ⁻⁴	318	

	ΔS^\ddagger	ΔH^\ddagger
For Pt(FHPy) HH \rightarrow HT	-29 J Mol ⁻¹ K ⁻¹	84 KJ Mol ⁻¹
For Pt(FHPy) HT \rightarrow HH	16 J Mol ⁻¹ K ⁻¹	105 KJ Mol ⁻¹

a. Temperature = 298 K

b. Pyridine concentration is a constant

Table 9 shows the rate constants and activation parameters of Pt(FHPy) interconversion.

Proton NMR spectroscopy has been used to identify and follow the interconversion of Pt(FHPy) (HH \rightleftharpoons HT) in CDCl₃.

Kinetic study of the reaction is based on the rate law, $-d[HH]/dt = k_f[HH] - k_r([HH]_o - [HH])$. With the assumption that

pyridine concentration is much larger than the HH Pt(III) complex concentration, so that Py functions as a constant. One sets up the model for $\text{HH} \rightleftharpoons \text{HT}$, an approach to equilibrium expression for which $K_{\text{eq}} = k_f/k_r$, $[\text{HT}] = [\text{HH}]_0 - [\text{HH}]$. The time dependence of the decrease of the HH Pt(III) complex concentration and the appearance and increase of the HT Pt(III) complex concentration, with the addition of the free pyridine, fit the integrated form of the rate law which describes the pseudo first-order approach:

$$-d[\text{HH}]/dt = k_f[\text{HH}] - k_r([\text{HH}]_0 - [\text{HH}])$$

$$\text{Integrated form: } \ln(k_f[\text{HH}]_0 / \{(k_f + k_r)[\text{HH}] - k_r[\text{HH}]_0\})$$

$$= (k_f + k_r)t$$

$$\text{At equilibrium: } d[\text{HH}]/dt = 0$$

$$k_f[\text{HH}]_{\text{eq}} = k_r([\text{HH}]_0 - [\text{HH}]_{\text{eq}})$$

$$[\text{HH}]_{\text{eq}} = k_r[\text{HH}]_0 / (k_f + k_r)$$

Substitution into the integrated form result:

$$\ln([\text{HH}]_0 - [\text{HH}]_{\text{eq}} / [\text{HH}] - [\text{HH}]_{\text{eq}}) = (k_f + k_r)t$$

Therefore $-\ln([HH]-[HH]_{eq})$ vs. time should result in a straight line if analysis is correct. The slope of this straight line is k_f+k_r and one can determine the rate constant by the following equations if the equilibrium constant for the interconversion is known.

$$K = k_f / k_r$$

$$\text{slope} = k_f + k_r$$

Recently a similar HH to HT rearrangement was studied in a very different system (66). In the Pt(II) complexes studied hydroxypyridine bridge breakage and formation were involved. Similar kinetic models and equations were used. Unlike the system we studied, there were no Pt-Pt bonds nor were axial ligands present in product or reactant. The data obtained from that study should be compared to our data for the HT \rightleftharpoons HH reaction. As that system was studied in water, while our reaction was carried out in chloroform, detailed comparison is unreasonable. Nevertheless, comparison of their results to ours for the HT to HH interconversion is illuminating. In both results, the activation entropy is consistent with a dissociative concerted mechanism for bridge isomerization.

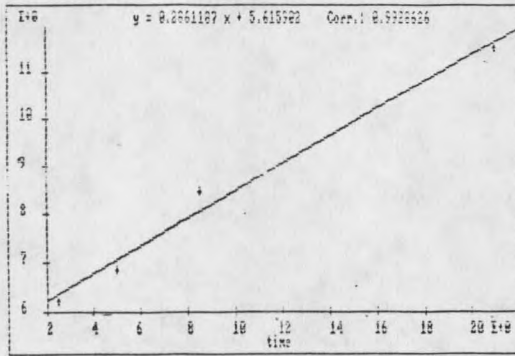
The changes of the reaction rate of HH Pt(III) complex on NMR spectra are directly proportional to the changes in concentration of pyridine. The higher the concentration of pyridine, the faster the increase of HT peak height forms on

NMR spectra and the quicker the final equilibrium is reached (Figure 14).

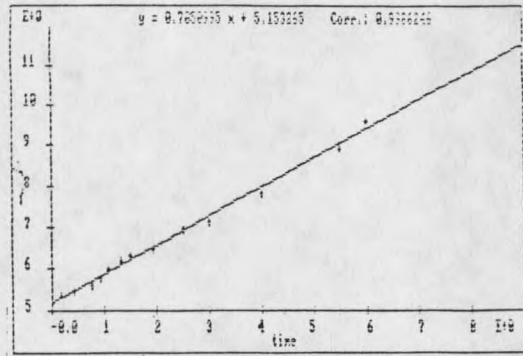
The changes of reaction rate of HH Pt(III) complexes are also related to the temperature. The higher the temperature, the faster the reaction goes (Figure 15).

The different temperature measurement for the interconversion determines the reaction activation enthalpy and activation entropy using Eyring plot (Figure 16).

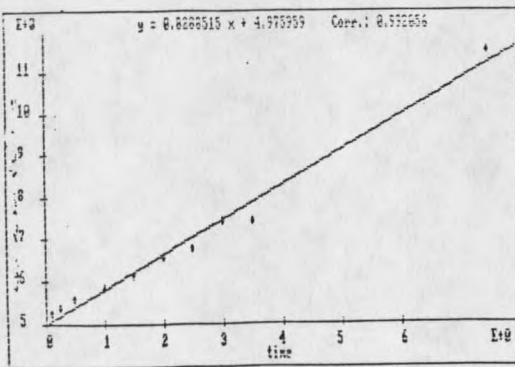
Rate studies reveal the reaction rate is greatly influenced by the concentration of pyridine and temperature. Reaction at varying pyridine concentrations established that the reaction is first order in pyridine and first order in HH complex. Addition of free hydroxypyridine to the reaction mixture showed no formation of a mixed HPy, FHPy platinum complex even after 20 half-lives for the HH to HT rearrangement. These facts taken together suggest one of two mechanisms. In route 1, a preequilibrium in which pyridine binds the HH complex is followed by a rate determining step, which involves a somewhat dissociative but concerted rearrangement of an FHPy bridge (Figure 17). In route 2, pyridine attacks in a rate determining associative step displacing one bond to the FHPy bridge. The FHPy bridge subsequently converts to form an HT complex (Figure 18). The possibility of a mechanism involving rupture of the metal-metal bond was also considered. Theoretically,



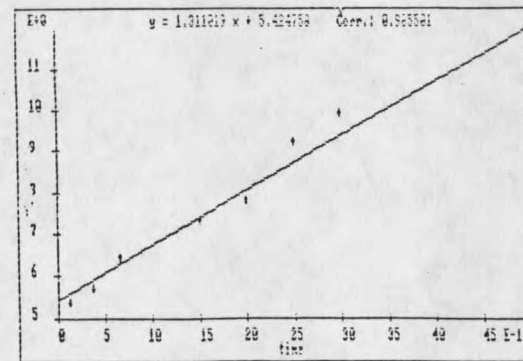
-Ln([HH]-[HH]_{eq}) vs. Time (hours)
[Py]=10 μL T=296K



-Ln([HH]-[HH]_{eq}) vs. Time (Hours)
[Py]=20 μL T=296K

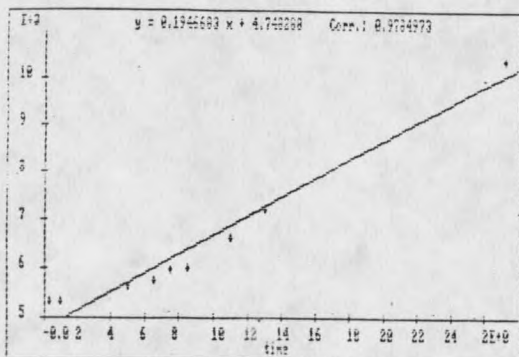


-Ln([HH]-[HH]_{eq}) vs. Time (hours)
[Py]=25 μL T=296K

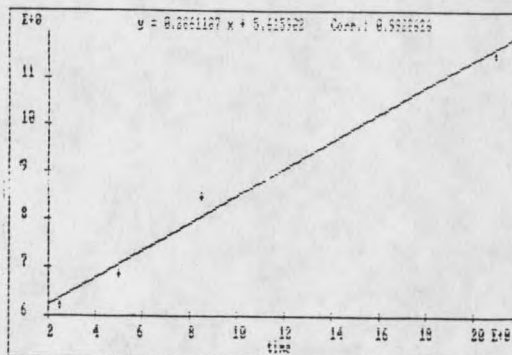


-Ln([HH]-[HH]_{eq}) vs. Time (hours)
[Py]=50 μL T=296K

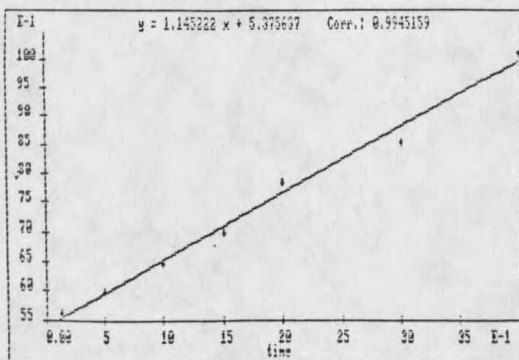
Figure 14. $-\text{Ln}[(\text{HH})-(\text{HH})_{\text{eq}}]$ vs. time (hours) plot
Pt(FHPy) $\text{HH} \rightarrow \text{HT}$ at different pyridine
concentrations



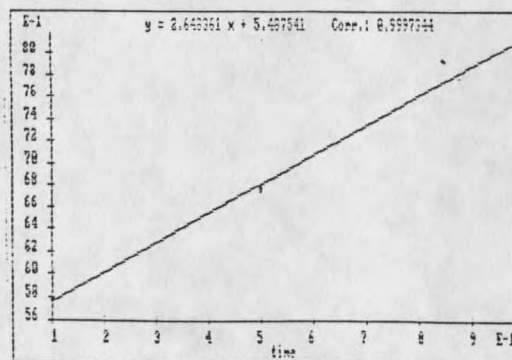
$-\ln([HH]-[HH]_{eq})$ vs. Time (hours)
[Py]=10 μ L T=283K



$-\ln([HH]-[HH]_{eq})$ vs. Time (hours)
[Py]=10 μ L T=296K

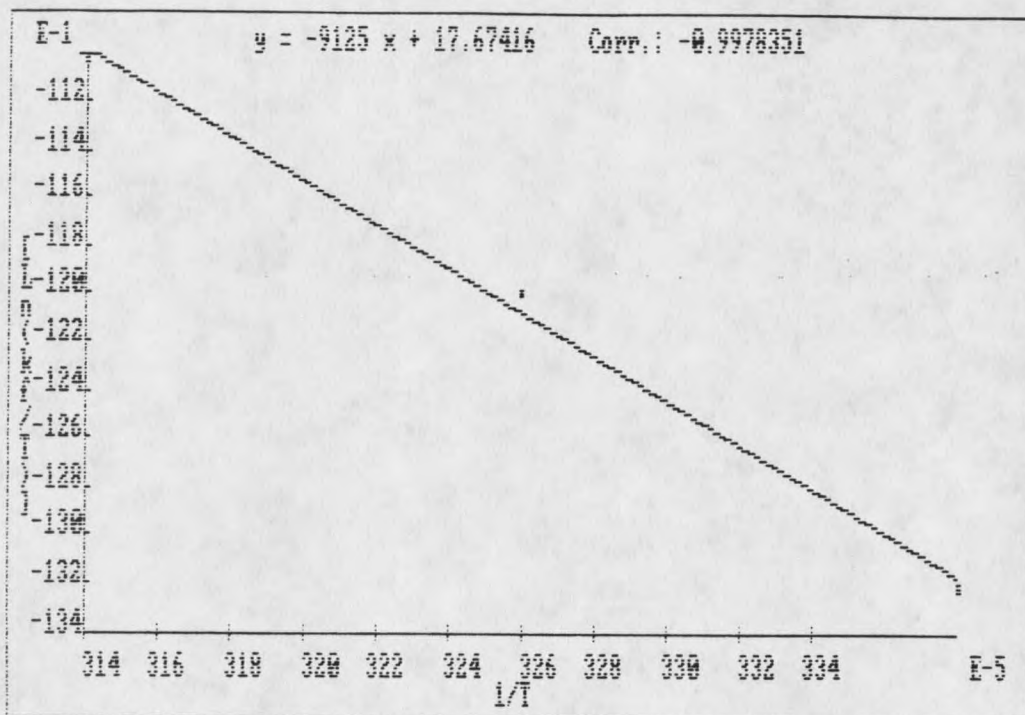


$-\ln([HH]-[HH]_{eq})$ vs. Time (hours)
[Py]=10 μ L T=307K



$-\ln([HH]-[HH]_{eq})$ vs. Time (hours)
[Py]=10 μ L T=318K

Figure 15. $-\ln([HH]-[HH]_{eq})$ vs. time (hours) plot
Pt(FHPy) $HH \rightarrow HT$ at different temperatures



$\ln(k/T)$ vs. $1/T$

Figure 16. Eyring plot for Pt(FHPy) HH \rightarrow HT

