



The synthesis, analysis, and characterization of a group of platinum clusters  
by Eric Spencer Peterson

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:

There is a great deal of interest in the synthesis of materials which possess special physical and chemical properties. One such area of interest is concerned with the formation and chemistry of platinum-platinum bonds. The structures of platinum-platinum bonded species which exhibit the platinum(III) oxidation state have only recently been elucidated. The chemical pathways leading to the platinum(III) oxidation state are not well understood. Presented here is structural evidence for what is considered to be one of the initial steps in the pathway leading to platinum-platinum bonds. Two single crystal x-ray crystal structures exhibiting a bent nitrosyl ligand upon a monomeric platinum center are presented. To our knowledge, no other examples of bent nitrosyl ligands on platinum monomeric species exist in current literature. The single crystal x-ray crystallographic structures of three closely related complexes are also presented. ESCA studies, visible spectral and infrared spectral studies are also presented in support of the structural data. Additionally, the results of NMR and ESCA studies of a group of structurally related platinum(III) dimeric complexes are presented. The NMR data include complete sets of  $^{195}\text{Pt}$ ,  $^{13}\text{C}$ , and  $^1\text{H}$  spectral information. Generally, the solid state structure was found to remain intact in solution. Unusually large platinum-platinum coupling constants were observed during the course of the investigations. The ESCA studies of the same platinum-platinum bonded species lend support to the platinum(III) oxidation state. Finally, the synthesis, analysis, and chemical characterization of a group of tetrameric platinum-platinum bonded complexes is presented.

A newly developed synthetic scheme for the tetrameric complexes, along with an efficient method of chromatographic purification of the complexes is presented. Single crystal x-ray crystallographic information is presented about a new structural derivative of the octakisacetato platinum complex. The complex exhibits a pair of bridging carbonyl ligands on opposite sides of the tetrameric rectangle, and a pair of asymmetric bridging acetate ions trans to the carbonyl ligands. The short sides of the tetrameric rectangle are bridged by symmetric acetate ions. Infrared, visible, ESCA and elemental analytic studies are presented as evidence for the complexes. A novel application of NMR determining the total number of acetate ligands per cluster is also presented. Eighteen other derivatives of the octakisacetato tetrameric complex were made using different ligands. The reaction conditions under which the complexes were found to react appear unique for this set of complexes. Infrared, visible, ESCA and elemental analytic data are presented in support of the proposed structures for the complexes.

The possible oxidation states of each of the complexes is considered. It is hoped that this work will aid in future systematic synthetic efforts for exploratory studies of platinum-platinum bonded compounds.

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

of

Doctor of Philosophy

in

Chemistry

MONTANA STATE UNIVERSITY  
Bozeman, Montana

December 1987

D378  
P4425

APPROVAL

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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DEDICATION

To Mom and Dad.

## ACKNOWLEDGMENTS

I would like to thank Dr. Edwin H. Abbott for his advice. I would also like to thank all of those people who have made my stay in graduate school quite pleasant.

## TABLE OF CONTENTS

	<u>Page</u>
LIST OF TABLES . . . . .	x
LIST OF FIGURES . . . . .	xiv
KEY ABBREVIATIONS . . . . .	xvii
ABSTRACT . . . . .	.xviii
INTRODUCTION . . . . .	1
Sulfate and Phosphate Bridged Species . . . . .	6
$\alpha$ -Oxopyridonate Bridged Platinum(III) Complexes . . . . .	11
Platinum Carboxylate Bridged Compounds . . . . .	14
PURPOSE OF THE PRESENT INVESTIGATION . . . . .	20
EXPERIMENTAL . . . . .	22
Preparation of Compounds . . . . .	22
Preparation of $K_2Pt(NO_2)_4 \cdot H_2O$ . . . . .	22
Preparation of $K_2Pt(NO_2)_4(NO)(H_2O)$ , <u>1</u> . . . . .	22
Method II for the Preparation of $K[Pt(NO_2)_4NO \cdot OH_2] \cdot OH_2$ , <u>1</u> , with $NOBF_4$ . . . . .	23
Preparation of $K_2[Pt(Cl_3)(NO_2)_2NO]$ , <u>2</u> . . . . .	23
Preparation of $K_2[Pt(NO_2)_2Cl_4]$ , <u>3</u> . . . . .	23
Method II for Preparation of $K_2[Pt(NO_2)_2Cl_4]$ , <u>3</u> . . . . .	25
Preparation of $K_2[Pt(NO_2)_4Br_2]$ , <u>4</u> . . . . .	25
Preparation of $K_2[Pt(PO_3)_2Cl_2]$ , <u>5</u> . . . . .	25
Preparation of $Pt_4(OAc)_8$ Blue from Platinum(IV) . . . . .	26
Synthesis of $Pt_4(OAc)_8$ from Platinum(II), <u>10</u> . . . . .	27
Preparation of $[Pt_4(OAc)_6(CO)_2] \cdot 2HOAc$ , <u>6</u> . . . . .	28
Direct Preparation of $[Pt_4(OAc)_6(CO)_2]$ $\cdot 2HOAc$ , <u>6</u> , from $Pt_4(OAc)_8$ Blue . . . . .	28
Direct Method I for the Preparation of <u>6</u> Using Formic Acid . . . . .	28
Direct Method II for the Preparation of <u>6</u> Using Co Gas . . . . .	30
Direct Preparation of $[Pt_4(OAc)_6(NO)_2]$ $\cdot 2HOAc$ , <u>12</u> . . . . .	30



## TABLE OF CONTENTS (continued)

	<u>Page</u>
Direct Method I for the Preparation of <u>12</u> Using Nitric Acid . . . . .	31
Direct Method II for the Preparation of <u>12</u> Using NO Gas. . . . .	31
Preparation of $[\text{Pt}_2(\text{POP})_4 \cdot \text{H}_2\text{O}]$ from $\text{Pt}_4(\text{OAc})_8$ Blue, <u>13</u> . . . . .	32
Preparation of $\text{Pt}_2(\text{POP})_4 \cdot \text{H}_2\text{O}$ from $\text{Pt}_4(\text{OAc})_8$ Blue with Ammonium Diphosphite, <u>13</u> . . . . .	32
Reaction of $\text{Pt}_4(\text{OAc})_8$ Blue with KOCN . . . . .	33
Reaction of $\text{Pt}_4(\text{OAc})_8$ Blue with 20 Equivalents KOCN, <u>14</u> . . . . .	33
Reaction of $\text{Pt}_4(\text{OAc})_8$ Blue with 20 Equivalents KSCN, <u>15</u> . . . . .	33
Reaction of $\text{Pt}_4(\text{OAc})_8$ Blue with Eight Equivalents KSCN, <u>16</u> . . . . .	34
Reaction of $\text{Pt}_4(\text{OAc})_8$ Blue with Four Equivalents KSCN, <u>17</u> . . . . .	35
Reaction of $\text{Pt}_4(\text{OAc})_8$ Blue with Two Equivalents KSCN, <u>18</u> . . . . .	35
Reaction of $\text{Pt}_4(\text{OAc})_8$ Blue with Acetylene Gas, <u>19</u> . . . . .	36
Reaction of $\text{Pt}_4(\text{OAc})_8$ Blue with Phenylacetylene, <u>20</u> . . . . .	36
Reaction of $\text{Pt}_4(\text{OAc})_8$ Blue with Diphenylacetylene, <u>21</u> . . . . .	38
Reaction of $\text{Pt}_4(\text{OAc})_8$ Blue with One Equivalent Triphenylphosphine, <u>22</u> . . . . .	39
Reaction of $\text{Pt}_4(\text{OAc})_8$ Blue with Two Equivalents Triphenylphosphine, <u>23</u> . . . . .	39
Reaction of $\text{Pt}_4(\text{OAc})_8$ Blue with Four Equivalents Triphenylphosphine, <u>24</u> . . . . .	40
Reaction of $\text{Pt}_4(\text{OAc})_8$ Blue with Excess HCN, <u>25</u> . . . . .	40
Reaction of $\text{Pt}_4(\text{OAc})_8$ Blue with HCN Controlled Reaction, <u>26</u> . . . . .	41
Reaction of $\text{Pt}_4(\text{OAc})_8$ Blue with One and Two Equivalents of Cyanamide, <u>27</u> . . . . .	42
Reaction of $\text{Pt}_4(\text{OAc})_8$ Blue with Eight Equivalents of Acetamide, <u>28</u> . . . . .	42
Reaction of $\text{Pt}_4(\text{OAc})_8$ Blue with Trifluoroacetic Acid, <u>29</u> . . . . .	43
Reaction of $\text{Pt}_4(\text{OAc})_8$ Blue with Sulfuric Acid, <u>30</u> . . . . .	43
Reaction of $\text{Pt}_4(\text{OAc})_8$ Blue with $\text{K}_2\text{SO}_4$ , <u>31</u> . . . . .	44
Reaction of $\text{Pt}_4(\text{OAc})_8$ Blue with Eight Equivalents Hydroxypyridine, <u>32</u> . . . . .	44

## TABLE OF CONTENTS (continued)

	<u>Page</u>
Materials and Methods. . . . .	45
Chromatographic Procedures . . . . .	46
Preparation of Ag Salts. . . . .	47
NMR Spectroscopy of Pt(III) Dimeric Species. . . . .	47
X-Ray Crystallography. . . . .	51
Structure Solution of $K[Pt(NO_2)_4(NO)(H_2O)] \cdot H_2O$ , <u>1</u> . . . . .	52
Structure Solution for $K_2[Pt(NO_2)_2(NO)Cl_3]$ , <u>2</u> . . . . .	55
Structure Solution for $K_2[Pt(NO_2)_4Br_2]$ , <u>3</u> . . . . .	58
Structure Solution for $K_2[Pt(NO_2)_2Cl_4]$ , <u>4</u> . . . . .	58
Structure Solution for $K_2[Pt(Cl)_2(PO_3)_2]$ , <u>5</u> . . . . .	60
Structure Solution for $[Pt_4(OAc)_6(CO)_2] \cdot 2HOAc$ , <u>6</u> . . . . .	63
RESULTS . . . . .	65
X-Ray Crystallographic Results . . . . .	65
Structure of $K[Pt(NO_2)_4(NO)(OH_2)]$ , <u>1</u> . . . . .	65
Structure of $K_3[Pt(NO_2)_2(NO)(Cl)_3]$ , <u>2</u> . . . . .	69
Structure of $K_2[Pt(NO_2)_2Cl_4]$ , <u>3</u> . . . . .	74
Structure of $K_2[Pt(NO_2)_4Br_2]$ , <u>4</u> . . . . .	76
Structure of $K_2[Pt(Cl)_2(PO_3)_2]$ , <u>5</u> . . . . .	79
Structure of $[Pt_4(OAc)_6(CO)_2] \cdot 2(HOAc)$ , <u>6</u> . . . . .	82
Physical Measurements. . . . .	88
Electron Spectroscopy for Chemical Analysis (ESCA). . . . .	88
NMR Spectra and Spectral Assignments for a Series of Pt(III) Complexes. . . . .	91
Infrared Spectral Results. . . . .	130
Total Ligands Per Metal Cluster Determination. . . . .	143
Results of Elemental Analyses of Selected Compounds. . . . .	143

## TABLE OF CONTENTS (continued)

	<u>Page</u>
DISCUSSION. . . . .	150
Synthetic Procedures . . . . .	162
Reactivity Studies . . . . .	164
Structural Studies . . . . .	165
NMR Studies. . . . .	169
ESCA Studies . . . . .	173
Infrared Spectral Studies. . . . .	176
Elemental Analytical Studies . . . . .	181
Proposed Structures. . . . .	182
SUMMARY . . . . .	188
REFERENCES CITED. . . . .	191
APPENDIX. F <sub>O</sub> F <sub>C</sub> Tables for Compounds <u>1</u> - <u>6</u> . . . . .	197

## LIST OF TABLES

<u>Table</u>	<u>Page</u>
1. Crystallographic parameters for $K[Pt(NO_2)_4(NO)(H_2O)] \cdot H_2O$ , <u>1</u> . . . . .	53
2. Crystallographic parameters for $K[Pt(NO_2)_2(NO)Cl_3]$ , <u>2</u> . . . . .	56
3. Crystallographic parameters for $K_2Pt(NO_2)_4Br_2$ , <u>3</u> . . . . .	59
4. Crystallographic parameters for $K_2[Pt(NO_2)_2Cl_4]$ , <u>4</u> . . . . .	61
5. Crystallographic parameters for $K_2[PtCl_2(PO_3)_2]$ , <u>5</u> . . . . .	62
6. Crystallographic parameters for $[Pt_4(OOCCH_3)_6(CO)_2]$ , <u>6</u> . . . . .	64
7. Atomic coordinates ( $\times 10^4$ ) and isotropic thermal parameters ( $\text{\AA}^2 \times 10^3$ ) for $K[Pt(NO_2)_4(NO)OH_2] \cdot (OH_2)$ . . . . .	66
8. Bond lengths ( $\text{\AA}$ ) for $K[Pt(NO_2)_4(NO)OH_2] \cdot (OH_2)$ . . . . .	67
9. Bond angles ( $^\circ$ ) for $K[Pt(NO_2)_4(NO)OH_2] \cdot (OH_2)$ . . . . .	68
10. Anisotropic thermal parameters ( $\text{\AA} \times 10^3$ ) for $K[Pt(NO_2)_4(NO)OH_2] \cdot (OH_2)$ . . . . .	69
11. Atomic coordinates ( $\times 10^4$ ) and isotropic thermal parameters ( $\text{\AA} \times 10^3$ ) for $K_2[Pt(NO_2)_2(NO)Cl_3]$ . . . . .	71
12. Bond lengths ( $\text{\AA}$ ) for $K_2[Pt(NO_2)_2(NO)Cl_3]$ . . . . .	71
13. Bond angles ( $^\circ$ ) for $K_2[Pt(NO_2)_2(NO)Cl_3]$ . . . . .	72
14. Anisotropic thermal parameters ( $\text{\AA}^2 \times 10^3$ ) for $K_2[Pt(NO_2)_2(NO)Cl_3]$ . . . . .	73
15. Atomic coordinates ( $\times 10^4$ ) and isotropic thermal parameters ( $\text{\AA}^2 \times 10^3$ ) for $K_2[Pt(NO_2)_2Cl_4]$ . . . . .	75

## LIST OF TABLES (continued)

<u>Table</u>	<u>Page</u>
16. Bond lengths (Å) for $K_2[Pt(NO_2)_2Cl_4]$ . . . . .	75
17. Bond angles (°) for $K_2[Pt(NO_2)_2Cl_4]$ . . . . .	75
18. Anisotropic thermal parameters ( $\text{Å}^2 \times 10^3$ ) for $K_2[Pt(NO_2)_2Cl_4]$ . . . . .	76
19. Atomic coordinates ( $\times 10^4$ ) and isotropic thermal parameters ( $\text{Å}^2 \times 10^3$ ) for $K_2[Pt(NO_2)_2Cl_4]$ . . . . .	77
20. Bond lengths (Å) for $K_2[Pt(NO_2)_2Cl_4]$ . . . . .	77
21. Bond angles (°) for $K_2[Pt(NO_2)_2Cl_4]$ . . . . .	78
22. Anisotropic thermal parameters ( $\text{Å}^2 \times 10^3$ ) for $K_2[Pt(NO_2)_4Br_2]$ . . . . .	78
23. Atomic coordinates ( $\times 10^4$ ) and isotropic thermal parameters ( $\text{Å}^2 \times 10^3$ ) for $K_2[Pt(PO_3)_2Cl_2]$ . . . . .	80
24. Bond lengths (Å) for $K_2[Pt(PO_3)_2Cl_2]$ . . . . .	81
25. Bond angles (°) for $K_2[Pt(PO_3)_2Cl_2]$ . . . . .	81
26. Anisotropic thermal parameters ( $\text{Å}^2 \times 10^3$ ) for $K_2[Pt(PO_3)_2Cl_2]$ . . . . .	82
27. Atomic coordinates ( $\times 10^4$ ) and isotropic thermal parameters ( $\text{Å}^2 \times 10^3$ ) for $[Pt_4(OAc)_6(CO)_2 \cdot 2(HOAc)]$ . . . . .	84
28. Bond lengths (Å) for $[Pt_4(OAc)_6(CO)_2 \cdot 2(HOAc)]$ . . . . .	85
29. Bond angles (°) for $[Pt_4(OAc)_6(CO)_2 \cdot 2(HOAc)]$ . . . . .	86
30. Anisotropic thermal parameters ( $\text{Å}^2 \times 10^3$ ) for $[Pt_4(OAc)_6(CO)_2 \cdot 2(HOAc)]$ . . . . .	88
31. ESCA data for platinum complexes . . . . .	90
32. $Pt_2(mhp)_2(CH_3)_4(pyr)_1$ (head-to-head dimer) . . . . .	93
33. $Pt_2(CH_3)_4(hp)_2(Et_2S)_1$ (head-to-head dimer) . . . . .	98
34. $Pt_2(CH_3)_4(mhp)_2(Et_2S)_1$ (head-to-head dimer). . . . .	102
35. $Pt_2(CH_3)_4(fhp)_2(pyr)_2$ (head-to-tail dimer) . . . . .	106

## LIST OF TABLES (continued)

<u>Table</u>	<u>Page</u>
36. $\text{Pt}_2(\text{CH}_3)_4(\text{chp})_2(\text{pyr})_1$ (head-to-head dimer) . . . . .	110
37. $\text{Pt}_2(\text{CH}_3)_4(\text{fhp})_2(\text{Et}_2\text{S})_1$ (head-to-head dimer). . . . .	115
38. $\text{Pt}_2(\text{CH}_3)_4(\text{fhp})_2(\text{pyr})_1$ (head-to-head dimer) . . . . .	119
39. $\text{Pt}_2(\text{CH}_3)_4(\text{hp})_2(\text{pyr})_2$ (head-to-tail dimer) and $\text{Pt}_2(\text{CH}_3)_4(\text{hp})_2(\text{pyr})_1$ (head-to-head dimer). . . . .	124
40. Infrared spectral results for $\text{K}[\text{Pt}(\text{NO}_2)_4(\text{NO})(\text{OH}_2)] \cdot \text{OH}_2$ , <u>1</u> . . . . .	130
41. Infrared spectral results for $\text{K}[\text{Pt}(\text{NO}_2)_2\text{Cl}_3(\text{NO})]$ , <u>2</u> . . . . .	130
42. Infrared spectral results for $\text{Pt}_4(\text{OAc})_6(\text{CO})_2$ , purple fraction, <u>6</u> . . . . .	131
43. Infrared spectral results for $\text{Pt}_4(\text{OAc})_8$ , blue fraction, <u>7</u> , <u>10</u> . . . . .	131
44. Infrared spectral results for $\text{Pt}_4(\text{OAc})_8$ , green fraction, <u>8</u> . . . . .	132
45. Infrared spectral results for reaction of $\text{Pt}_4(\text{OAc})$ blue and $\text{NOBF}_4$ or $\text{NO}$ (gas) or $\text{HNO}_3$ , two equivalents (purple solid), <u>12</u> . . . . .	132
46. Infrared spectral results for reaction of $\text{Pt}_4(\text{OAc})_8$ blue and $\text{KOCN}$ , 10 and 20 equivalents, <u>14</u> . . . . .	133
47. Infrared spectral results for reaction of $\text{Pt}_4(\text{OAc})_8$ blue and $\text{KSCN}$ , 20 equivalents, <u>15</u> . . . . .	133
48. Infrared spectral results for reaction of $\text{Pt}_4(\text{OAc})_8$ blue and eight equivalents $\text{KSCN H}_2\text{O}$ insoluble fraction, <u>16</u> . . . . .	134
49. Infrared spectral results for reaction of $\text{Pt}_4(\text{OAc})_8$ blue and four equivalents $\text{KSCN H}_2\text{O}$ soluble fraction, <u>17S</u> . . . . .	134
50. Infrared spectral results for reaction of $\text{Pt}_4(\text{OAc})$ blue and four equivalents $\text{KSCH H}_2\text{O}$ insoluble fraction, <u>17I</u> , <u>18I</u> . . . . .	135

## LIST OF TABLES (continued)

<u>Table</u>	<u>Page</u>
51. Infrared spectral results for reaction of $\text{Pt}_4(\text{OAc})_8$ blue and $\text{KSCN}$ (two equivalents), <u>18S</u> . . . . .	135
52. Infrared spectral results for reaction of $\text{Pt}_4(\text{OAc})_8$ blue and $\text{HC}\equiv\text{CH}$ (gas), <u>19</u> . . . . .	136
53. Infrared spectral results for $\text{Pt}_4(\text{OAc})$ blue and phenylacetylene, <u>20</u> . . . . .	136
54. Infrared spectral results for reaction of $\text{Pt}_4(\text{OAc})$ blue and $\text{PhC}\equiv\text{PCh}$ , <u>21</u> . . . . .	137
55. Infrared spectral results for reaction of $\text{Pt}_4(\text{OAc})_8$ and $(\text{PH}_3\text{P})$ , two and four equivalents, <u>23</u> , <u>24</u> . . . . .	137
56. Infrared spectral results for reactions of $\text{Pt}_4(\text{OAc})_8$ blue and $\text{HCN}$ or $\text{KCN}$ , two equivalents, <u>26</u> . . . . .	138
57. Infrared spectral results for $\text{Pt}_4(\text{OAc})_8$ blue plus cyanamide, one and two equivalents, <u>27</u> . . . . .	138
58. Infrared spectral results for $\text{Pt}_4(\text{OAc})_8$ blue with eight equivalents acetamide, <u>28</u> . . . . .	139
59. Infrared spectral results for $\text{Pt}_4(\text{OAc})_8$ blue with trifluoroacetic acid, <u>29</u> . . . . .	139
60. Infrared spectral results for $\text{Pt}_4(\text{OAc})_8$ blue with $\text{H}_2\text{SO}_4$ , <u>30</u> . . . . .	140
61. Infrared spectral results for reaction of $\text{Pt}_4(\text{OAc})_8$ blue and excess $\text{K}_2\text{SO}_4$ , <u>31</u> . . . . .	140
62. Visible spectroscopic measurements . . . . .	141
63. Determination of total ligands per cluster by $^1\text{H}$ NMR. . . . .	144
64. Results of elemental analyses. . . . .	147
65. Proposed formulae, supporting data, and proposed structures for all of the platinum complexes presented. . . . .	184

## LIST OF TABLES (continued)

<u>Table</u>	<u>Page</u>
66. $F_O F_C$ Tables for $F_K[Pt(NO_2)_4(NO)H_2O] \cdot H_2O$ , <u>1</u> . . . . .	197
67. $F_O F_C$ Tables for $K_2[Pt(NO_2)_2(NO)Cl_3]$ , <u>2</u> . . . . .	240
68. $F_O F_C$ Tables for $K_2[Pt(NO_2)_2(Br)_2]$ , <u>3</u> . . . . .	271
69. $F_O F_C$ Tables for $K_2[Pt(NO_2)_2Cl_4]$ , <u>4</u> . . . . .	280
70. $F_O F_C$ Tables for $K_2[Pt(Cl)_2(PO_3)_2]$ , <u>5</u> . . . . .	286
71. $F_O F_C$ Tables for $[Pt_4(OAc)_6(CO)_2] \cdot 2HOAc$ , <u>6</u> . . . . .	317



## LIST OF FIGURES

<u>Figure</u>	<u>Page</u>
1. The reaction sequence leading to the dimeric platinum(III) phosphate and sulfate complexes. . . . .	8
2. Oxopyridonate ligands and their derivatives. . . . .	12
3. (a) Head-to-head configuration. (b) Head-to-tail configuration . . . . .	12
4. The octakisacetatoplatinum(II) complex which is of interest in this investigation . . . . .	15
5. The newer, somewhat safer synthesis of the oktakisacetatoplatinum(II) complex . . . . .	18
6. The preparation of the octakisacetatoplatinum(II) complexes in this study. . . . .	19
7. Synthetic schemes for compounds <u>1-5</u> . . . . .	24
8. Synthetic schemes for compounds <u>6-8</u> . . . . .	29
9. Synthetic scheme for compounds <u>19-32</u> . . . . .	37
10. ORTEP view of $K[Pt(NO_2)_4(NO)(OH_2)] \cdot OH_2$ , <u>1</u> . . . . .	66
11. ORTEP view of $K_2[Pt(NO_2)_2(NO)(Cl)_3]$ , <u>2</u> . . . . .	70
12. ORTEP view of $K_2[Pt(NO_2)_2Cl_4]$ , <u>3</u> . . . . .	74
13. ORTEP view of $K_2[Pt(NO_2)_4Br_2]$ , <u>4</u> . . . . .	76
14. ORTEP view of $K_2[Pt(Cl)_2(PO_3)_2]$ , <u>5</u> . . . . .	80
15. ORTEP view of $[Pt_4(OAc)_6(CO)_2] \cdot 2(HOAc)$ , <u>6</u> . . . . .	83
16. The molecular numbering scheme used for this investigation: a) head-to-head platinum(III) dimer; b) head-to-tail platinum(III) dimer. . . . .	92
17. $^1H$ NMR spectrum of $[Pt_2(CH_3)_4(mhp)_2(pyr)]$ . . . . .	94

## LIST OF FIGURES (continued)

<u>Figure</u>	<u>Page</u>
18. $^{13}\text{C}(^1\text{H})$ NMR spectrum of $[\text{Pt}_2(\text{CH}_3)_4(\text{mhp})_2(\text{pyr})]$ . . . . .	95
19. Upfield region of $^{195}\text{Pt}$ NMR spectrum of $[\text{Pt}_2(\text{CH}_3)_4(\text{mhp})_2(\text{pyr})]$ . . . . .	96
20. Downfield region of $^{195}\text{Pt}$ NMR spectrum of $[\text{Pt}_2(\text{CH}_3)_4(\text{mhp})_2(\text{pyr})]$ . . . . .	97
21. Figure 21. $^1\text{H}$ NMR spectrum of $[\text{Pt}_2(\text{CH}_3)_4(\text{hp})_2(\text{C}_2\text{H}_5)_2\text{S}]$ . . . . .	99
22. $^{13}\text{C}(^1\text{H})$ NMR spectrum of $[\text{Pt}_2(\text{CH}_3)_4(\text{hp})_2((\text{C}_2\text{H}_5)_2\text{S})]$ . . . . .	100
23. $^{195}\text{Pt}$ NMR spectrum of $[\text{Pt}_2(\text{CH}_3)_4(\text{hp})_2((\text{C}_2\text{H}_5)_2\text{S})]$ . . . . .	101
24. $^1\text{H}$ NMR spectrum of $[\text{Pt}_2(\text{CH}_3)_4(\text{mhp})_2((\text{C}_2\text{H}_5)_2\text{S})]$ . . . . .	103
25. $^{13}\text{C}(^1\text{H})$ NMR spectrum of $[\text{Pt}_2(\text{CH}_3)_4(\text{mhp})_2((\text{C}_2\text{H}_5)_2\text{S})]$ . . . . .	104
26. $^{195}\text{Pt}$ NMR spectrum of $[\text{Pt}_2(\text{CH}_3)_4(\text{mhp})_2((\text{C}_2\text{H}_5)_2\text{S})]$ . . . . .	105
27. $^1\text{H}$ NMR spectrum of $[\text{Pt}_2(\text{CH}_3)_4(\text{fhp})_2(\text{pyr})_2]$ . . . . .	107
28. $^{13}\text{C}(^1\text{H})$ NMR spectrum of $[\text{Pt}_2(\text{CH}_3)_4(\text{fhp})_2(\text{pyr})_2]$ . . . . .	108
29. $^{195}\text{Pt}$ NMR spectrum of $[\text{Pt}_2(\text{CH}_3)_4(\text{fhp})_2(\text{pyr})_2]$ . . . . .	109
30. $^1\text{H}$ NMR spectrum of $[\text{Pt}_2(\text{CH}_3)_4(\text{chp})_2(\text{pyr})]$ . . . . .	111
31. $^{13}\text{C}(^1\text{H})$ NMR spectrum of $[\text{Pt}_2(\text{CH}_3)_4(\text{chp})_2(\text{pyr})]$ . . . . .	112
32. Upfield region of $^{195}\text{Pt}$ NMR spectrum of $[\text{Pt}_2(\text{CH}_3)_4(\text{chp})_2(\text{pyr})]$ . . . . .	113
33. Downfield region of $^{195}\text{Pt}$ NMR spectrum of $[\text{Pt}_2(\text{CH}_3)_4(\text{chp})_2(\text{pyr})]$ . . . . .	114
34. $^1\text{H}$ NMR spectrum of $[\text{Pt}_2(\text{CH}_3)_4(\text{fhp})_2((\text{C}_2\text{H}_5)_2\text{S})]$ . . . . .	116
35. $^{13}\text{C}(^1\text{H})$ NMR spectrum of $[\text{Pt}_2(\text{CH}_3)_4(\text{fhp})_2((\text{C}_2\text{H}_5)_2\text{S})]$ . . . . .	117
36. $^{195}\text{Pt}$ NMR spectrum of $[\text{Pt}_2(\text{CH}_3)_4(\text{fhp})_2((\text{C}_2\text{H}_5)_2\text{S})]$ . . . . .	118
37. $^1\text{H}$ NMR spectrum of $[\text{Pt}_2(\text{CH}_3)_4(\text{fhp})_2(\text{pyr})]$ . . . . .	120
38. $^{13}\text{C}(^1\text{H})$ NMR spectrum of $[\text{Pt}_2(\text{CH}_3)_4(\text{fhp})_2(\text{pyr})]$ . . . . .	121

## LIST OF FIGURES (continued)

<u>Figure</u>	<u>Page</u>
39. Upfield region of $^{195}\text{Pt}$ spectrum of $[\text{Pt}_2(\text{CH}_3)_4(\text{fhp})_2(\text{pyr})]$ . . . . .	122
40. Downfield region of $^{195}\text{Pt}$ NMR spectrum of $[\text{Pt}_2(\text{CH}_3)_4(\text{fhp})_2(\text{pyr})]$ . . . . .	123
41. $^1\text{H}$ NMR spectrum of $[\text{Pt}_2(\text{CH}_3)_4(\text{hp})_2(\text{pyr})_2]$ . . . . .	126
42. $^{13}\text{C}(^1\text{H})$ NMR spectrum of $[\text{Pt}_2(\text{CH}_3)_4(\text{hp})_2(\text{pyr})_2]$ . . . . .	127
43. Upfield region of $^{195}\text{Pt}$ NMR spectrum of $[\text{Pt}_2(\text{CH}_3)_4(\text{hp})_2(\text{pyr})_2]$ . . . . .	128
44. Downfield region of $^{195}\text{Pt}$ NMR spectrum of $[\text{Pt}_2(\text{CH}_3)_4(\text{hp})_2(\text{pyr})_2]$ . . . . .	129
45. Hypothetical mechanism for the generation of a nitrosyl complex. a) The protonation of the nitrito-group; b) displacement of the NO group; c) our proposed oxidative addition of the NO ligand to the platinum(II) species (33) . . . . .	154
46. Head-to-tail dimeric platinum(III) arrangement showing the two types (I and II) of methyls on opposite platinum ions . . . . .	159
47. Synthesis of the derivative species and their compound numbers as presented in this discussion . . . . .	183

## KEY ABBREVIATIONS

Å	=	Angstroms
chp	=	Chlorohydroxypyridine
DN	=	Downfield
ESCA	=	Electron Spectroscopy for Chemical Analysis (X. P. S.)
Et	=	Ethyl
Et <sub>2</sub> S	=	Diethyl Sulfide [(H <sub>5</sub> C <sub>2</sub> ) <sub>2</sub> S]
E <sub>b</sub>	=	Binding energy
eV	=	Electron volts
fhp	=	Fluorohydroxypyridine
H Form	=	Formic acid
H <sub>2</sub> NOC <sub>2</sub> H <sub>3</sub>	=	Acetamide
HOAc	=	Acetic acid
hp	=	Hydroxypyridine
Hz	=	Hertz
Me	=	Methyl
mhp	=	Methylhydroxypyridine
MHz	=	Megahertz
nm	=	Nanometers
NCN <sup>-</sup>	=	Cyanamide
NMR	=	Nuclear Magnetic Resonance
OAc <sup>-</sup>	=	Acetate ion
OCN <sup>-</sup>	=	Cyanate ion
ppm	=	Parts per million
Pt	=	Platinum
pyr	=	Pyridine
SCN <sup>-</sup>	=	Thiocyanate ion
TPP	=	Triphenylphenylphosphine
UP	=	Upfield
v	=	Frequency
X	=	Halogen, or <u>specified functional group</u>
Y	=	<u>Specified functional group</u>

## ABSTRACT

There is a great deal of interest in the synthesis of materials which possess special physical and chemical properties. One such area of interest is concerned with the formation and chemistry of platinum-platinum bonds. The structures of platinum-platinum bonded species which exhibit the platinum(III) oxidation state have only recently been elucidated. The chemical pathways leading to the platinum(III) oxidation state are not well understood. Presented here is structural evidence for what is considered to be one of the initial steps in the pathway leading to platinum-platinum bonds. Two single crystal x-ray crystal structures exhibiting a bent nitrosyl ligand upon a monomeric platinum center are presented. To our knowledge, no other examples of bent nitrosyl ligands on platinum monomeric species exist in current literature. The single crystal x-ray crystallographic structures of three closely related complexes are also presented. ESCA studies, visible spectral and infrared spectral studies are also presented in support of the structural data. Additionally, the results of NMR and ESCA studies of a group of structurally related platinum(III) dimeric complexes are presented. The NMR data include complete sets of  $^{195}\text{Pt}$ ,  $^{13}\text{C}$ , and  $^1\text{H}$  spectral information. Generally, the solid state structure was found to remain intact in solution. Unusually large platinum-platinum coupling constants were observed during the course of the investigations. The ESCA studies of the same platinum-platinum bonded species lend support to the platinum(III) oxidation state. Finally, the synthesis, analysis, and chemical characterization of a group of tetrameric platinum-platinum bonded complexes is presented. A newly developed synthetic scheme for the tetrameric complexes, along with an efficient method of chromatographic purification of the complexes is presented. Single crystal x-ray crystallographic information is presented about a new structural derivative of the octakisacetato platinum complex. The complex exhibits a pair of bridging carbonyl ligands on opposite sides of the tetrameric rectangle, and a pair of asymmetric bridging acetate ions trans to the carbonyl ligands. The short sides of the tetrameric rectangle are bridged by symmetric acetate ions. Infrared, visible, ESCA and elemental analytic studies are presented as evidence for the complexes. A novel application of  $^1\text{H}$  NMR determining the total number of acetate ligands per cluster is also presented. Eighteen other derivatives of the octakisacetato tetrameric complex were made using different ligands. The reaction conditions under which the complexes were found to react appear unique for this set of complexes. Infrared, visible, ESCA and elemental analytic data are presented in support of the proposed structures for the complexes. The possible oxidation states of each of the complexes is considered. It is hoped that this work will aid in future systematic synthetic efforts for exploratory studies of platinum-platinum bonded compounds.

## INTRODUCTION

For 3000 years platinum has fascinated man (1). This interest stems from his recognition that platinum is a relatively rare element, occurring only in specific mineral deposits. These deposits are scattered in a mere handful of locations throughout our world, including the U.S.S.R., South Africa, South America, and Montana (2). A number of theories abound concerning the origins of the minerals which bear the platinum metals. One of the most highly publicized theories suggests these deposits originated with meteorite impacts on the earth's surface (3). Whatever the origins of such minerals, modern man has certainly been able to enjoy the resulting chemical characteristics which the platinum metals offer. The following discussion examines one of these characteristics of platinum chemistry: platinum-platinum bond formation.

Before proceeding with the discussion, a brief review of man's fascination with the platinum metals is in order. This fascination has existed for some 30 centuries; an Egyptian casket found at Thebes, dating from the seventh century B.C., contained an alloy of platinum, iridium and gold (4). There was, however, no evidence suggesting that the alloy of platinum was to the Egyptians anything more than a workable precious metal. Eight hundred years later, during the first century A.D., Pliny discussed platinum, known then as cassiteros or plumbum candidum. Pliny suggested the following:

It is now known that cassiteros is a product of Lucitania, and Gallaecia. It is a sand found on the surface of the earth, and of a black color, can be detected only by its weight.... It is also found in the gold mines that are known as Alutice or Talutice, the stream of water which is passed through then detaches certain black pebbles, mottled with small white spots and of the same weight (density) as gold. Hence it is that they remain with gold in the baskets in which it is collected; and being separated in the furnace, are then melted, and become converted into album plumbum (5).

Other than this scanty knowledge, very little was really learned about the platinum family for centuries; however, there are a number of accounts of the mysterious "platina" metal found throughout some of the early literature (6). During the sixteenth century, J. C. Scaliger noted that there was a non-fusible metallic substance in the mines of Mexico and Darian (Panama) which did not melt in the Spanish gold smelting furnaces. Current thought is that the described substance was probably platinum, simply because platinum is known to occur in these very areas. During the middle of the eighteenth century, A. deUlloa accompanied the expedition sent from France to measure the arc of the meridian of the equator, and in his account of the voyage he mentioned that in the mines of El Chaco', Columbia, South America, there was an unworkable metallic stone which the Spanish called "platina" and which made gold ores useless if it were associated in large quantities (7). The Spanish considered the platina useless and commonly threw the platina into the rivers of South America.

The study of platinum began in earnest in 1741 when W. Brownigg received a specimen of native platina from C. Wood, a metallurgist in

Jamaica, who claimed that he had obtained the sample from Carthogina, New Grenada. A number of other platina samples began to find their way to Europe at about the same time and were examined by several different investigators (8). A number of theories sprouted, concerning both what the metal was and what its specific properties were. These were published in the metallurgical/ chemical literature of the period (9).

Some decades later, during April 1803, R. Chenevix received an anonymous circular to the effect that a new metal called palladium could be purchased at Forster's of Gerrard Street, Soho, London (10). The "new" metal had some very specific properties which were previously unknown for virtually any other element. Chenevix believed this to be a fraud; he bought up the entire stock and, after investigating the question, concluded that the substance was not a new element but rather a platinum amalgam of peculiar properties (11). Following Chenevix's publication at the Royal Society May 3, 1803, there appeared an advertisement offering a reward to anyone who could prepare a grain of the new substance, either by Chenevix's method or any other (12). Though no one succeeded in securing the reward, in 1804 W. H. Wallaston announced the discovery of a new element in platinum ore. Between 1804 and 1828 the other members of the platinum metal family were isolated and purified (1804--palladium, rhodium, iridium, osmium; 1828--ruthenium) (13).

The chemical exploration of the platinum metals began almost simultaneously and has, in the opinion of this author, proven to be



quite a significant segment of the transition metal chemical literature. Much of the earliest literature concerning the chemical properties of the platinum metals resulted from simply questioning what would be the resultant compounds (and their chemical properties) upon combination with a plethora of metals and ligands. Descriptions of alloys of platinum with copper, mercury, uranium, iron, and other platinum metals began to appear in the literature as early as the 1840's (14). Additionally, reports of some of the earliest coordination/cluster complexes began to appear at roughly the same time. These early efforts were made using both simple ligands, such as  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ ,  $\text{OH}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{PO}_4^{2-}$ , and a number of much more complicated ligands (14). The only analytic method employed by many of the chemists was elemental analysis and generally a substantial amount of reaction chemistry. Of course, the chemist's eyes were also a very valuable analytic tool and provided a significant amount of the information which one observes in the literature, even to this day.

Studying the literature both old and relatively recent yields discovery of a number of complexes which reportedly contain polynuclear metal centers. These complexes are investigated for a number of reasons; a few of the major areas of interest follow:

- 1) biological activity of clusters;
- 2) electronic applications of clusters;
- 3) catalytic activity;

- 4) structure bonding relationships; and
- 5) systematic chemical properties;

Each of the above areas has a significant amount of literature associated with it; however, a review of such a broad spectrum of chemistry is inappropriate at this time. Nonetheless, the question of just what a platinum cluster is needs clarification. For the purposes of this dissertation, a platinum cluster will be defined as being two or more platinum atoms which are brought together either by the "bite" size of a ligand or by the formation of a platinum-platinum bond. Of course, the more interesting cases occur when a metal-metal bond is formed or broken due to the chemical interactions involved in such processes. Examples vary from relatively simple dimeric species which exhibit platinum-platinum bonds, through groups of trimeric, tetrameric, and one-dimensional polymeric species. Such examples only begin to touch upon the complexity with which the coordination chemist must attempt to cope.

Our interest in the platinum metal clusters has centered on developing the type of systematic chemistry that can be performed upon the clusters either in the formation or destruction of the platinum metal clusters themselves. To initiate this, we have set about investigating the chemistry of platinum-platinum bonded species. Our approach has been guided by several areas of specific interest which follow:

- 1) synthesis;
- 2) disproportionation reactions;

- 3) substitution reactions;
- 4) cluster redox chemistry; and
- 5) mechanistic considerations.

Reading the following pages will reveal that each of the five areas above will be addressed, either as a route to compounds, or as a method for the analysis of such complexes.

The initial portion of this work was undertaken to investigate the reaction chemistry of a group of binuclear platinum(III) complexes. Such binuclear  $d^7-d^7$  metal complexes possess a net single bond between the metal atoms and exhibit an electronic configuration of  $\sigma^2\pi^4\delta^2\delta^*2\pi^*4$  (15). Generally the systems have two or four ligands bridging the metal centers and possess axial positions which can be occupied by appropriate monodentate ligands. Such a style of bonding and electronic configuration is observed in  $Rh_2 +4$  systems (16-18), for which several examples have been structurally characterized. By comparison, however, the  $Pt_2 +6$  systems have only recently been studied in any detail, and few structural examples are known.

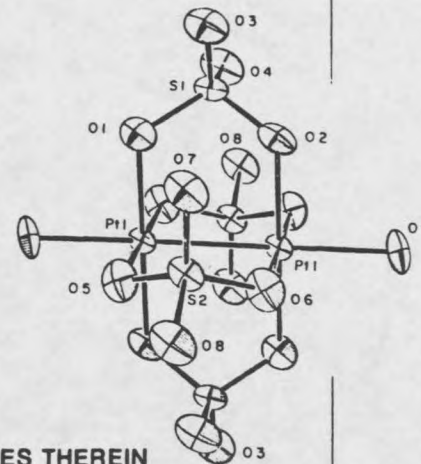
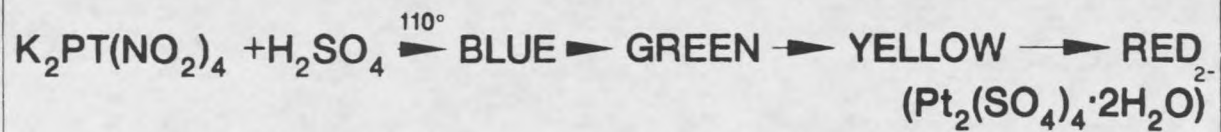
#### Sulfate and Phosphate Bridged Species

In 1905 Blondel prepared a complex which he suggested was a platinum(III) complex. This complex was the first example of such an oxidation state and still elicits questions about the electronic configuration of the metal atoms (19). In a complex reaction between platinum(IV) and an aqueous sulfuric acid solution which was reduced with oxalic acid, Blondel formed the binuclear platinum(III)

complex  $[\text{H}_2(\text{Pt}_2(\text{SO}_4)_4(\text{H}_2\text{O})_2)] \cdot 9.5\text{H}_2\text{O}$ . Additionally, Blondel reported the sodium and potassium salts of the complex (20). Blondel's work was confirmed several years later by Wöhler and Frey (21), who also synthesized several closely related species. The potassium salt which Blondel reported proved to be significant in that it was the first structurally characterized platinum(III) complex (22) exhibiting platinum-platinum bonds (23-27).

The reaction conditions under which the complexes are prepared appear quite simple. Essentially all that is required is heating a given platinum(II) complex with an aqueous solution of either sulfuric or phosphoric acid. During the course of the reaction, at least four color changes are observed, as is exhibited in Figure 1. The reaction begins as a colorless solution, changing sequentially to blue, green, yellow; then the dimeric red-orange product precipitates from solution. Our efforts to perform nuclear magnetic resonance (NMR) spectroscopic studies upon the product proved exceptionally difficult due, as we found, to the low solubility of the product in all solvents. Additionally, a group of Australians were at the same time completing the nuclear magnetic resonance studies of the complexes (29). Since our interests were focused both upon the study of platinum-platinum bonds and upon the processes which must take place to form the bonds, we decided to investigate the events which precede platinum-platinum bond formation. Given the idea (in inorganic chemistry) that one color of a solution can indicate a single compound, there is in the above system the potential for

SYNTHESIS OF Pt(III)'PO<sub>4</sub><sup>-</sup> AND SO<sub>4</sub><sup>2-</sup> DIMERS'



\*COTTON et al. INORGANIC CHEMISTRY (1982) 21 1709, AND REFERENCES THEREIN

Figure 1. The reaction sequence leading to the dimeric platinum(III) phosphate and sulfate complexes.

describing at least two or three complexes. In theory, describing such a series of events could give a "snapshot" view of the sequence of events which lead to the formation of platinum-platinum bonds and perhaps present some insights into the mechanism of platinum-platinum bond formation. Therefore, this line of research was pursued and is described herein. We were able to obtain a group of blue crystals which were formed in the early part of the reaction sequence described previously. These crystals proved to be highly air and moisture sensitive. For platinum there seem to be three general classes of blue compounds. The best known class consists of linear tetrameric complexes of mixed valence (30). A second class, lesser known but well-characterized, is mononuclear, most probably with a charge transfer band in the long wavelength part of the visible spectrum (31-32). The third class has but a single well-characterized example—a mononuclear, blue, paramagnetic platinum species with rather bulky electron donating ligands which possibly function to prevent the dimerization of the platinum centers (33). A number of studies have been reported upon the blue solution which forms when platinum(II) nitrites react with phosphoric and/or sulfuric acids (23,28,34-36). The blue solutions owe their color to an absorption band near 630 nm. Some investigators have suggested that the blue compounds are nitrosyl complexes, but no structural information has been available due to the difficulties encountered with handling the complexes. The two complexes which are described in the following discussion (blue and green) each exhibit a bent

nitrosyl ligand upon the platinum atom. Only one other example of a bent nitrosyl on a platinum center was previously structurally characterized (37). Both complexes were shown to be highly unstable to air, moisture, and elevated temperatures. Additionally, unless the crystals of each compound were kept in their mother liquor and stored at  $-20^{\circ}\text{C}$  under airless conditions, the reaction was observed to proceed toward the red dimeric platinum(III) product. The blue species is believed to be one of two species present in solution during the initial steps of the platinum-platinum bond formation reaction sequence. The other species is probably a platinum(II) species which results from the well-characterized hydrolysis reaction of  $\text{K}_2\text{Pt}(\text{NO}_2)_4 \cdot 2\text{H}_2\text{O}$  in aqueous acid solutions (38). Since these two complexes are the second and third structural examples of the bent nitrosyl ligand on a platinum center, they have given some interesting insight into the initial steps of platinum-platinum bond formation. The structural details of bent nitrosyls on platinum have also been of interest. During efforts to make analogues to the two new complexes, several closely related species were crystallized and their structures elucidated. Such compounds will also be discussed in light of their relationship to the formation of platinum-platinum bonds.

$\alpha$ -Oxopyridonate Bridged Platinum(III) Complexes

There have been a number of synthetic approaches for the preparation of complexes with the platinum ions in the formal +3 oxidation state; however, most approaches yield products which are insoluble, give poor chemical yields, or are not reproducible (as we observed in the formation of the binuclear sulfate and phosphate species). A synthetic approach for the preparation of binuclear platinum(III) complexes with properties including high yield, stability, and solubility has been suggested by Vrieze (39-40). Vrieze's method employs platinum(II) precursors which (by oxidative addition reactions) yield binuclear platinum(III) products. The method involves the use of silver(I) carboxylate salts, which have been shown to give the binuclear platinum(III) species. Such species possess many of the "desirable" properties described earlier. F. A. Cotton's research group has employed a variation of Vrieze's method to obtain a group of new and interesting platinum(III) complexes. The complexes contain hydroxypyridine ( $\alpha$ -pyridone) derivatives which are known to give some interesting coordination geometries, especially as bridging ligands. The asymmetric ligands (Figure 2), typically stabilize metal-metal bonds by bridging the two metal centers (41-42). Examples of such ligands playing an important role in the chemistry of metal-metal bonds are found in a number of cases ranging from quadruple bonds (Cr, Mo, W) to single bonds (Rh, Pt) (15).



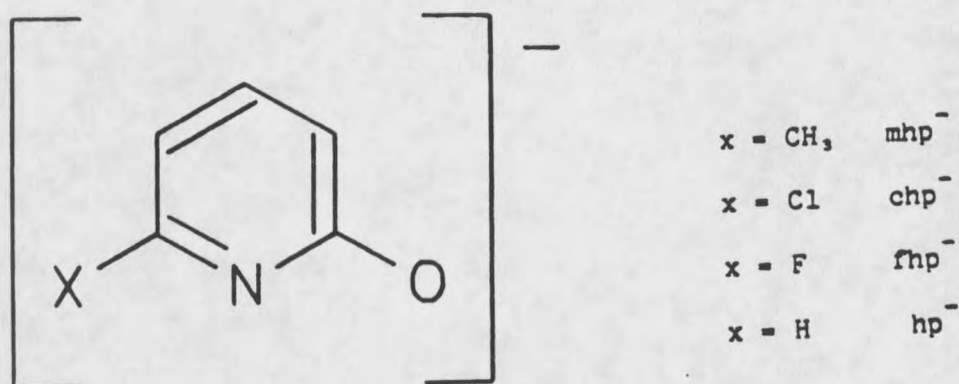


Figure 2. Oxopyridonate ligands and their derivatives.

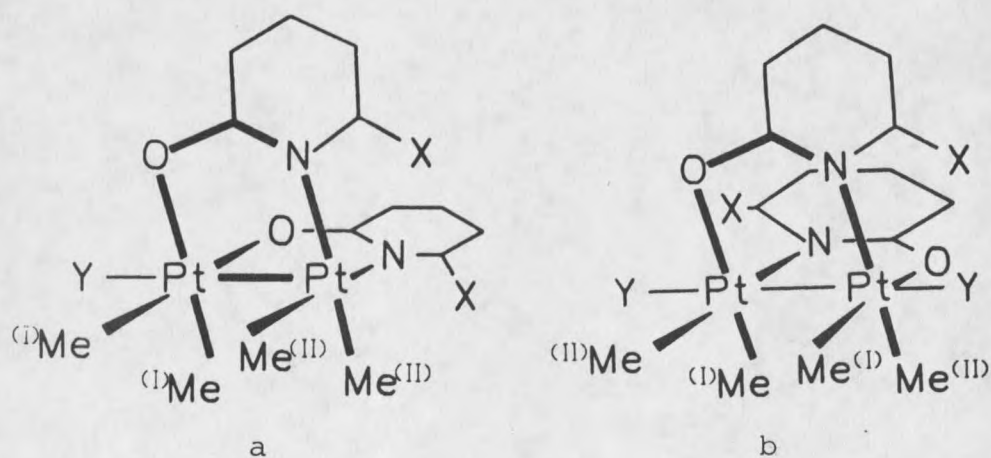
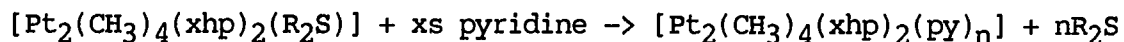
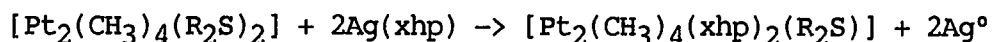


Figure 3. (a) Head-to-head configuration. (b) Head-to-tail configuration.

The resulting hydroxypyridinoate complexes have coordination geometries that are dependent upon the steric bulk of the substituted pyridine ring. If the substituent is large (e.g.,  $\text{Cl}^-$  or  $\text{CH}_3$ ), the complexes take the head-to-head bridging ligand arrangement, with one of the axial sites vacant due to the steric interference of the ring substituent (Figure 3). If, on the other hand, the substituent is relatively small (e.g., H or F), head-to-tail or head-to-head ligand arrangements can result. More interestingly, the complexes with the small substituents can inter-convert by the addition of an excess or the removal of the axial donor ligand (42). The preparation of the complexes follows the general scheme shown below:



where  $\text{R} = \text{C}_2\text{H}_5$ ;  $\text{x} = \text{H}, \text{F}, \text{Cl}, \text{Br}, \text{or } \text{CH}_3$ ; and  $n = 1 \text{ or } 2$ .

Using the above reaction sequences, Cotton's group has to date prepared ten new platinum(III) complexes, and they have structurally characterized the compounds by single crystal x-ray diffraction methods. Eight of the ten new complexes have been investigated by this author using nuclear magnetic resonance and x-ray photoelectron spectroscopic methods. In-solution structural details, NMR chemical shifts, and oxidation state information are reported here.

The platinum(III) complexes which were synthesized by Cotton's group are very stable in most organic solvents and can generally be isolated in high yield (70-90%). The NMR studies which appear here

suggest that the head-to-head complexes are stable in solution for relatively long periods of time, while the head-to-tail complexes tend to revert to equilibrium mixtures of head-to-head and head-to-tail forms over the course of a few hours to days. Evidence for interconversion is found in the platinum-195 NMR spectral data. Nonetheless, there is no evidence for the dissociation of the complexes in either case. Additional studies of the reaction chemistry of these complexes continues both here at Montana State University and in Cotton's group at Texas A and M University.

#### Platinum Carboxylate Bridged Compounds

Vreize's and Cotton's success with the formation of platinum-platinum bonds through oxidative additions of various carboxylato species to metal centers led us to investigate a tetrameric carboxylato species which had been characterized as being platinum(II). The complex exhibits an interesting structure (Figure 4). The structure is composed of a nearly planar square of four platinum ions, with each platinum ion being 2.5 Å from each of its nearest neighbors. There are bridging acetate ions between each of the metal centers, such that each metal center exhibits pseudo-octahedral coordination. The acetate ligands are alternately axial and equatorial on each side of the square; the resulting symmetry of the complex gives it quite an aesthetic appeal. Besides the aesthetic aspects of the complex, one notes that the 2.5 Å distance between the metal centers suggests platinum-platinum bonds. Such an









































































































































































































































































































































































































































































































































































































































































































































































































