



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  $\text{kJ Mol}^{-1}$ ) 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.  $^{31}\text{P}$  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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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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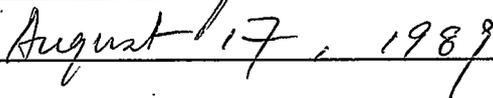
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To my dear Mom and Dad

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## KEY ABBREVIATIONS

Å	=	Angstroms
Et <sub>2</sub> S	=	Diethylsulfide [(H <sub>5</sub> C <sub>2</sub> ) <sub>2</sub> S]
Hz	=	Hertz
MHz	=	Megahertz
NMR	=	Nuclear Magnetic Resonance
ppm	=	part per million
Pt(HPy) (HH)	=	Pt <sub>2</sub> (CH <sub>3</sub> ) <sub>4</sub> (C <sub>5</sub> H <sub>4</sub> NO) <sub>2</sub> (Py)
Pt(HPy) (HT)	=	Pt <sub>2</sub> (CH <sub>3</sub> ) <sub>4</sub> (C <sub>5</sub> H <sub>4</sub> NO) <sub>2</sub> (Py) <sub>2</sub>
Pt(FHPy) (HH)	=	Pt <sub>2</sub> (CH <sub>3</sub> ) <sub>4</sub> (C <sub>5</sub> H <sub>3</sub> NOF) <sub>2</sub> (Py)
Pt(FHPy) (HT)	=	Pt <sub>2</sub> (CH <sub>3</sub> ) <sub>4</sub> (C <sub>5</sub> H <sub>3</sub> NOF) <sub>2</sub> (Py) <sub>2</sub>
Pt(ClHPy)	=	Pt <sub>2</sub> (CH <sub>3</sub> ) <sub>4</sub> (C <sub>5</sub> H <sub>3</sub> NOCl) <sub>2</sub> (Py)
Pt(MHPy)	=	Pt <sub>2</sub> (CH <sub>3</sub> ) <sub>4</sub> (C <sub>6</sub> H <sub>6</sub> NO) <sub>2</sub> (Py)
Pt(MHPy).Et <sub>2</sub> S	=	Pt <sub>2</sub> (CH <sub>3</sub> ) <sub>4</sub> (C <sub>6</sub> H <sub>6</sub> NO) <sub>2</sub> (Et <sub>2</sub> S)
Pt(MHPy).PPh <sub>3</sub>	=	Pt <sub>2</sub> (CH <sub>3</sub> ) <sub>4</sub> (C <sub>6</sub> H <sub>6</sub> NO) <sub>2</sub> (PPh <sub>3</sub> )
Pt dimer	=	K <sub>2</sub> [Pt <sub>2</sub> (NO <sub>2</sub> ) <sub>4</sub> (OH) <sub>2</sub> ]·1½H <sub>2</sub> O
Pt tetramer	=	K <sub>5</sub> [Pt <sub>4</sub> (NO <sub>2</sub> ) <sub>9</sub> (O) <sub>3</sub> ]·3H <sub>2</sub> 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  $\text{kJ Mol}^{-1}$ ) 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. Platinites in the complex are bonded to one another by oxo bridges. Three platinites 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.  $^{31}\text{P}$  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.

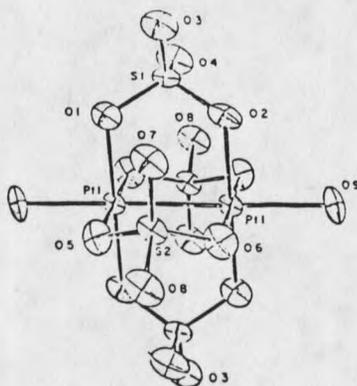
Because we are interested in making platinum compounds which have one or more Pt-Pt bonds, the basic understanding of the platinum oxidation states verses the electron configuration of the compound needs to be considered first.

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  $\text{Rh}^{+4}_2$  system (6-8) which is isoelectronic with the  $\text{Pt}^{+6}_2$  system. Numerous examples have been characterized structurally in the  $\text{Rh}^{+4}_2$  system.

Therefore one object of our work was to develop the methodology for the synthesis of  $\text{Pt}^{6+}_2$  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  $\text{Pt}_2^{6+}$  groups.

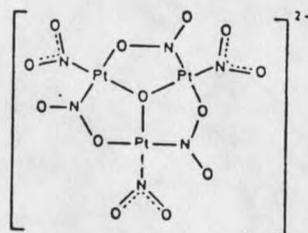
### Sulfate Bridged Compounds

In 1893 Veves reported that the reaction of dilute mineral acids with  $\text{K}_2[\text{Pt}(\text{NO}_2)_4]$  resulted in the formation of copper red needles (9, 10) which he formulated as  $\text{K}_2\text{H}_4\text{Pt}_3(\text{NO}_2)_6\text{O}\cdot 3\text{H}_2\text{O}$ . 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  $\text{K}[\text{Pt}(\text{SO}_4)_2]\cdot \text{H}_2\text{O}$ . 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  $\text{K}_2[\text{Pt}_2(\text{SO}_4)_4(\text{H}_2\text{O})_2]\cdot 9.5\text{H}_2\text{O}$ --a binuclear Pt(III) compound [1](13).



[1]

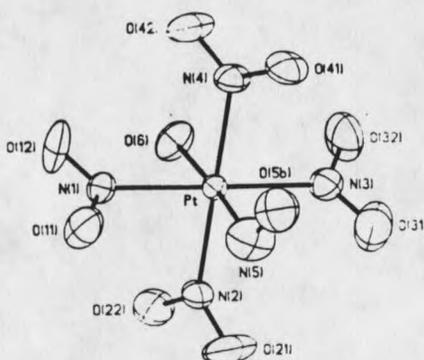
In 1977, new investigations of Vezes' red salt also reformulated the compound as  $K_2[Pt_3(NO_2)_6O] \cdot 3H_2O$  [2](14).



[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 H<sub>2</sub>O, 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(NO<sub>2</sub>)<sub>4</sub>(NO)(H<sub>2</sub>O)]·H<sub>2</sub>O [3](18).



[3]

A few derivatives of the sulfato-bridged platinum compound containing neutral or anionic axial ligands were also reported such as K<sub>2</sub>[Pt<sub>2</sub>(SO<sub>4</sub>)<sub>2</sub>(OSMe)<sub>2</sub>]·4H<sub>2</sub>O (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 K<sub>2</sub>Pt(NO<sub>2</sub>)<sub>4</sub> and H<sub>2</sub>SO<sub>4</sub> 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 [Re<sub>2</sub>(SO<sub>4</sub>)<sub>4</sub>(H<sub>2</sub>O)<sub>2</sub>]<sup>-4</sup> and [Mo<sub>2</sub>(SO<sub>4</sub>)<sub>4</sub>(H<sub>2</sub>O)<sub>2</sub>]<sup>-4</sup> that were characterized in the mid 70's

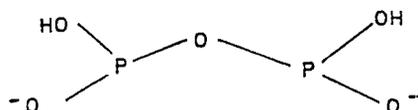
(15-16).

Phosphate and Pyrophosphite bridged complexes

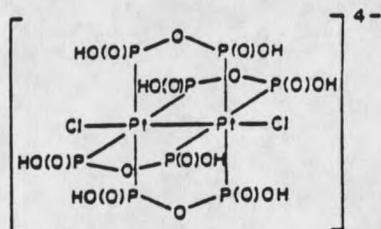
Binuclear platinum(III) phosphate compounds were discovered in 1980 (20). Their structures were determined shortly thereafter (21). The structure is very similar to that of sulfato bridged platinum complexes. The structure of the sulfate and phosphate complexes is referred to as a "lantern" structure. 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  $\sigma$  electrons in  $[\text{Pt}_2(\text{POP})_4]^{-4}$  in the  $\underline{\sigma^2\pi^4\delta^2\delta^{*2}\pi^*4\sigma^{*2}}$  electron configuration. The two antibonding  $\sigma$  electrons are transferred to the incoming  $\text{X}_2$  molecule in  $[\text{Pt}_2(\text{POP})_4\text{X}_2]^{-4}$  to form  $\underline{\sigma^2\pi^4\delta^2\delta^{*2}\pi^*4}$  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).



































































































































































































































































































































