



Synthesis, characterization, and mechanistic studies on a group of platinum complexes using  $^{195}\text{Pt}$  nuclear magnetic resonance  
by Danny Richard Bedgood, Jr

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 synthesis and reactions of three salts of a polymeric, intensely red luminescent platinum(II) complex formed by the reaction of  $\text{K}_2\text{PtCl}_6$  with  $\text{H}_3\text{P}_3\text{O}_3$  at  $220\text{--}240^\circ\text{C}$  are reported. The compound was characterized using  $^{31}\text{P}$  and  $^{195}\text{Pt}$  NMR, IR, UV/Vis and XPS spectroscopy, fluorometry, elemental analysis, and X-ray crystallography. The proposed structure has an average length of five platinum atoms per molecule and is a penta- anion, based upon elemental analysis data. NMR, IR, and UV/Vis spectroscopy support pyrophosphite bridges, with a pair of  $\text{P}(\text{OH})_3$  groups bound to each of the terminal platinum atoms, and the fluorometry data support a molecule with Pt-PT interactions based upon intense emission at  $659\text{nm}$ . Platinum XPS data indicate platinum(II) is present, although at  $72.6\text{eV}$  the resonance is slightly lower than for similar dimeric compounds. Crystals obtained from reactions with  $(\text{CH}_3)_4\text{NI}$  and  $(\text{CH}_3)_4\text{Br}$  and  $(\text{Bu})_4\text{NBr}$  were found to be  $\text{Pt}_2(\text{POP})_4\text{I}_2$  (cell dimensions  $16.0086, 16.8876, 16.3354\text{\AA}$ ) and  $\text{Pt}_2(\text{POP})_4\text{Br}_2$  (cell dimensions  $15.2880, 15.2921, 11.6217\text{\AA}$ ). Results of many reactions of the polymer with SCBT, CNT,  $\text{CH}_3\text{COOH}$ ,  $\text{HN}_3$ ,  $\text{H}_2\text{SO}_4$ ,  $\text{P}(\text{CsH}_5)_3$ , ethylenediamine, and other reagents are reported.

Studies on the polymerization of  $\text{Pt}(\text{OH})_6^{2-}$  in strong mineral acids is reported, and the formation of polymeric precipitates in  $\text{H}_2\text{SO}_4$ ,  $\text{H}_3\text{PO}_4$ ,  $\text{HClO}_4$ ,  $\text{HN}_3$ , and  $\text{CF}_3\text{SO}_3\text{H}$  are reported. Elemental analysis of the polymeric solids formed in  $\text{H}_2\text{SO}_4$  indicates 3-5 platinum atoms per anion and 12:1 for the  $\text{H}_3\text{PO}_4$  polymer. Formation of polymeric precipitates was not affected by reaction in non-aqueous media, and precipitates were obtained in various concentrations of platinum and acid (as long as acid concentration remained above  $0.1\text{M}$  [ $0.5\text{M}$  for  $\text{H}_3\text{PO}_4$ ] ).

A new synthetic scheme is described by which platinum(III) dimers can be formed by reaction of platinum(II) and platinum(IV), in the reverse of disproportionation.  $^{195}\text{Pt}$  NMR spectroscopy was used to follow the reactions, and identify the  $\text{Pt}_2(\text{SO}_4)_4^{2-}$  and  $\text{Pt}_2(\text{HP}_4)_4^{2-}$  products. This scheme was used to form a new compound with trifluoroacetic acid, proposed to be a platinum (III) dimer of the form  $\text{Pt}_2(\text{TFA})_4^{2+}$ . The formation and identification by  $^{195}\text{Pt}$  NMR spectroscopy of new platinum(II) and platinum(IV) complexes formed with trichloroacetic acid, methanesulfonic acid, and para-toluenesulfonic acid are also reported, with formation constants calculated for some of the platinum(II) species.

**SYNTHESIS, CHARACTERIZATION, AND MECHANISTIC STUDIES  
ON A GROUP OF PLATINUM COMPLEXES USING  
<sup>195</sup>PT NUCLEAR MAGNETIC RESONANCE**

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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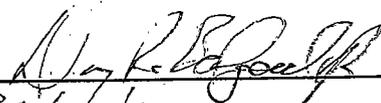
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## ABSTRACT

The synthesis and reactions of three salts of a polymeric, intensely red luminescent platinum(II) complex formed by the reaction of  $K_2PtCl_6$  with  $H_3PO_3$  at 220-240°C are reported. The compound was characterized using  $^{31}P$  and  $^{195}Pt$  NMR, IR, UV/Vis and XPS spectroscopy, fluorometry, elemental analysis, and X-ray crystallography. The proposed structure has an average length of five platinum atoms per molecule and is a penta-anion, based upon elemental analysis data. NMR, IR, and UV/Vis spectroscopy support pyrophosphite bridges, with a pair of  $P(OH)_3$  groups bound to each of the terminal platinum atoms, and the fluorometry data support a molecule with Pt-Pt interactions based upon intense emission at 659nm. Platinum XPS data indicate platinum(II) is present, although at 72.6eV the resonance is slightly lower than for similar dimeric compounds. Crystals obtained from reactions with  $(CH_3)_4NI$  and  $(CH_3)_4Br$  and  $(Bu)_4NBr$  were found to be  $Pt_2(POP)_4I_2$  (cell dimensions 16.0086, 16.8876, 16.3354Å) and  $Pt_2(POP)_4Br_2$  (cell dimensions 15.2880, 15.2921, 11.6217Å). Results of many reactions of the polymer with  $SCN^-$ ,  $CN^-$ ,  $CH_3COOH$ ,  $HNO_3$ ,  $H_2SO_4$ ,  $P(C_6H_5)_3$ , ethylenediamine, and other reagents are reported.

Studies on the polymerization of  $Pt(OH)_6^{2-}$  in strong mineral acids is reported, and the formation of polymeric precipitates in  $H_2SO_4$ ,  $H_3PO_4$ ,  $HClO_4$ ,  $HNO_3$ , and  $CF_3SO_3H$  are reported. Elemental analysis of the polymeric solids formed in  $H_2SO_4$  indicates 3-5 platinum atoms per anion and 12:1 for the  $H_3PO_4$  polymer. Formation of polymeric precipitates was not affected by reaction in non-aqueous media, and precipitates were obtained in various concentrations of platinum and acid (as long as acid concentration remained above 0.1M [0.5M for  $H_3PO_4$ ]).

A new synthetic scheme is described by which platinum(III) dimers can be formed by reaction of platinum(II) and platinum(IV), in the reverse of disproportionation.  $^{195}Pt$  NMR spectroscopy was used to follow the reactions, and identify the  $Pt_2(SO_4)_4^{2-}$  and  $Pt_2(HPO_4)_4^{2-}$  products. This scheme was used to form a new compound with trifluoroacetic acid, proposed to be a platinum(III) dimer of the form  $Pt_2(TFA)_4^{2+}$ . The formation and identification by  $^{195}Pt$  NMR spectroscopy of new platinum(II) and platinum(IV) complexes formed with trichloroacetic acid, methanesulfonic acid, and paratoluenesulfonic acid are also reported, with formation constants calculated for some of the platinum(II) species.

## CHAPTER I

## INTRODUCTION

**History**

Platinum has been used as ornamentation since antiquity, at which time it was confused with silver; the Egyptians and South American Indians used platinum for jewelry, no doubt believing it to be silver(1). It was as a result of the exploration of the South American continent that platinum was introduced to Europe. Perhaps the first unofficial report was as early as 1558 by Scallinger describing an infusible metal from Mexico and Darien. The first official report of this element was in 1748 by Don Antonio de Ulloa, who referred to it in his papers following a trip to South America; he and his papers were captured by English privateers, and his observations came to the attention of the Royal Society(2). In 1750 William Watson related to the Society a communication from William Browning of a "semi-metal called Platina di Pinto" found in the Spanish West Indies(3).

While the chemistry of platinum is very rich and varied, it is the formation of binuclear and larger cluster complexes by platinum that is of particular interest in this work. Perhaps among the first such compounds proposed was by Blondel(4), who in 1905

reported a platinum(III) complex containing coordinated sulfate; while only the empirical formula was determined, this compound has attracted a great deal of interest the last twenty years, and will be discussed in more detail below.

Perhaps the first report of a bimetallic platinum complex was in 1925 by Tschugaev(5), who described a hydrazine derivative of a phenylisocyanide, in which two hydrazine molecules bridge between two platinum complexes (Figure 1); for  $X=Cl^-$ , the compound is red, but upon

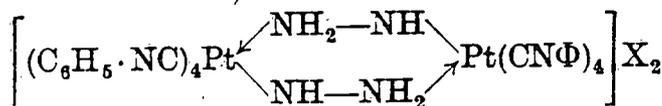


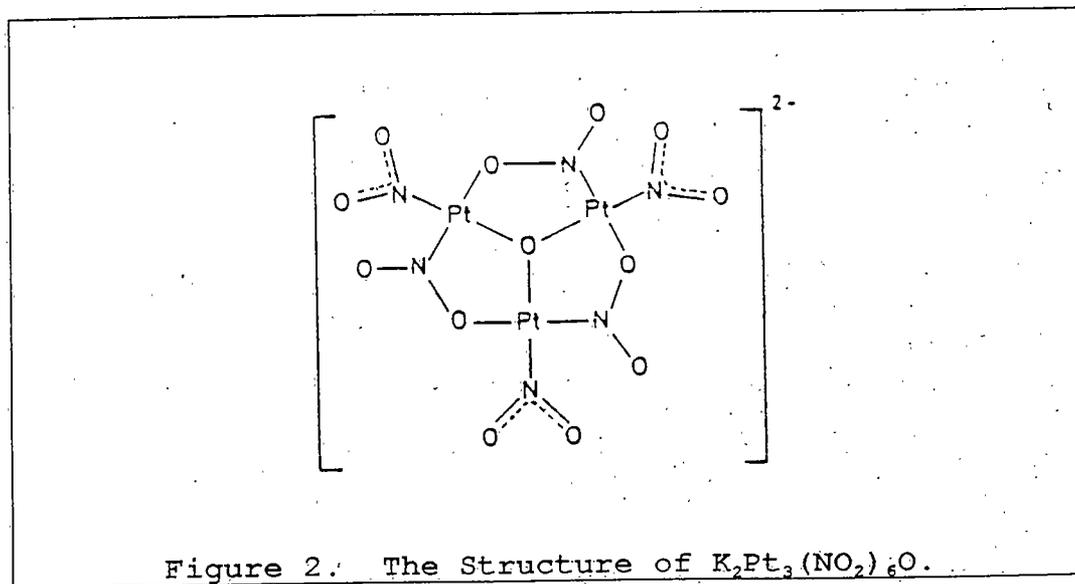
Figure 1. The Structure of  
 $[(C_6H_5NC)_4Pt(u-NH_2NH)_2Pt(CNC_6H_5)_4]X_2$ .

heating turns green, returning to red when cooled. Since that time many different types of binuclear (or larger) platinum clusters have been described and characterized with carbonyl (6) (7) (8) (9) (10), and carboxylate and dithiocarboxylate (11) (12) (13) (14) (15) (16) ligands, as well as the platinum blues (17) (18) (19) (20) (21) (22) (23) (24) (25) (26); of primary importance to the work described in this paper are the multinuclear platinum complexes formed with

sulfate, phosphate, pyrophosphite, and aquo/hydroxo ligands, described below.

### Sulfate Ligands

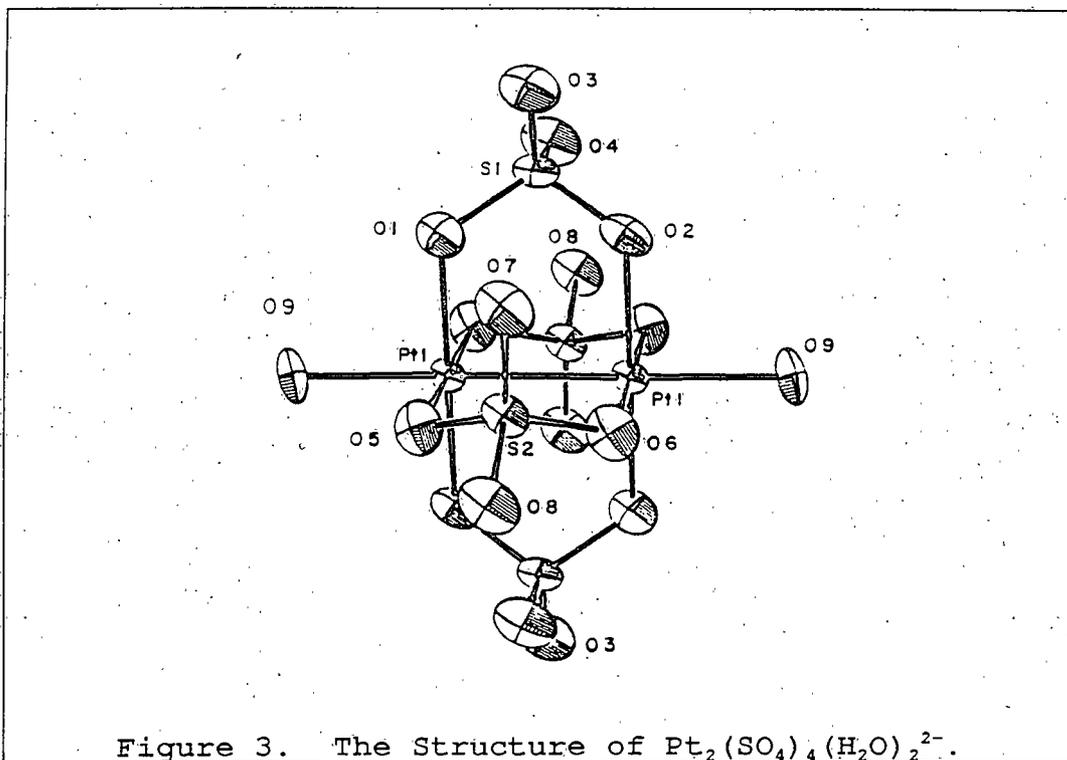
As mentioned above, Blondel reported that the reaction of  $\text{PtO}_2$  with concentrated sulfuric acid and oxalic acid reduction resulted in a compound that analyzed as  $\text{K}[\text{Pt}(\text{SO}_4)_2] \cdot \text{H}_2\text{O}$  (4). This was a modification of the reactions reported by Vezes in 1893 (27) (28), in which  $\text{K}_2\text{Pt}(\text{NO}_2)_4$  was reacted with dilute mineral acids to yield copper-red needles which he formulated as  $\text{K}_2\text{H}_4\text{Pt}_3(\text{NO}_2)_6 \cdot 3\text{H}_2\text{O}$  (reformulated in 1977 (29) as  $\text{K}_2[\text{Pt}_3(\text{NO}_2)_6\text{O}] \cdot 3\text{H}_2\text{O}$  with the structure shown in Figure 2.) Since the work by Blondel the



Russians have focused considerable attention upon the compound; in the first report of their work in this area, Ginzberg (30) prepared a compound like Blondel's by

reaction of  $\text{K}_2\text{Pt}(\text{NO}_2)_4$  with concentrated  $\text{H}_2\text{SO}_4$  to yield a compound proposed to contain platinum(III); a compound similar to this was reported from the reaction of  $\text{PtCl}_6^{2-}$  and sulfuric acid(31). The first formula proposed for the compound indicating multinuclearity was by Ivanova(32), who proposed a compound of the form  $\text{Pt}_2(\text{SO}_4)_4^{2-}$  based upon visible and infrared spectra on solvent extraction experiments with aqueous sulfate. Substitution of the proposed axial water molecules by halides, hydroxide, and nitrite was reported in 1975 (33) (34), one year before the crystal structure was determined (35). This work had attracted the attention of Cotton's group, who published a slightly revised synthesis(36) (37), and detailed crystal analysis(38) which resulted in the structure shown in Figure 3 (the first detailed crystal structure of the bimetallic platinum core was reported by Falohon of a DMSO derivative in 1982(39)).

Note the 'lantern' arrangement of the bridging ligands around the platinum core, and the axially coordinated water molecules; the molecule has essentially  $\text{C}_{4h}$  symmetry, for the O-Pt-Pt-O atoms fall in a plane with the sulfur atoms deviating consistently from that plane. The Pt-Pt bond distance is  $2.461\text{\AA}$ , indicating strong interaction between the metal atoms designated as a single bond. Several analogous compounds have now been

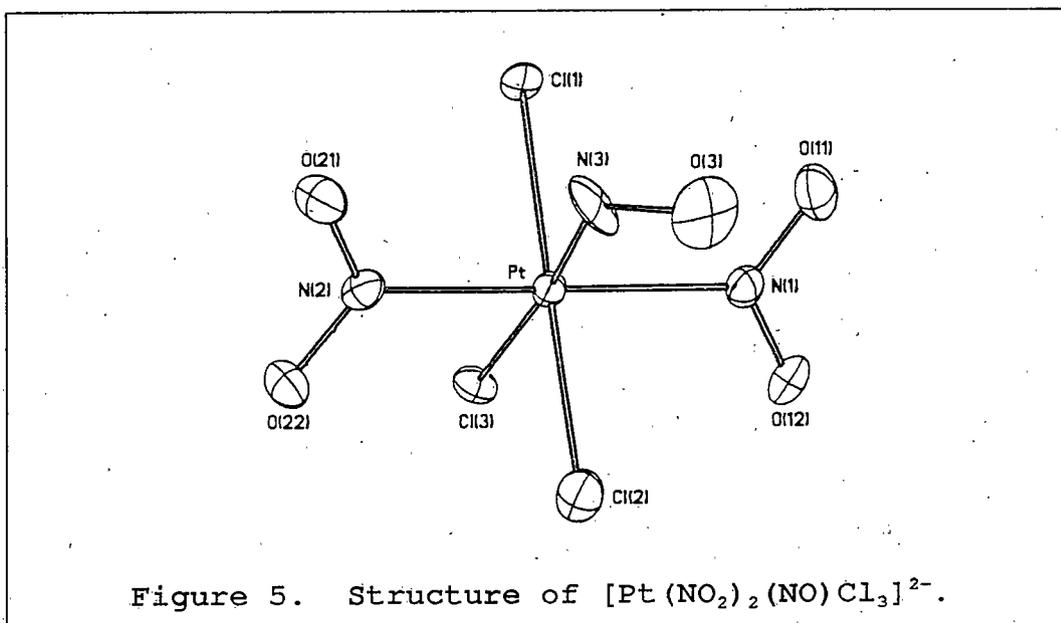
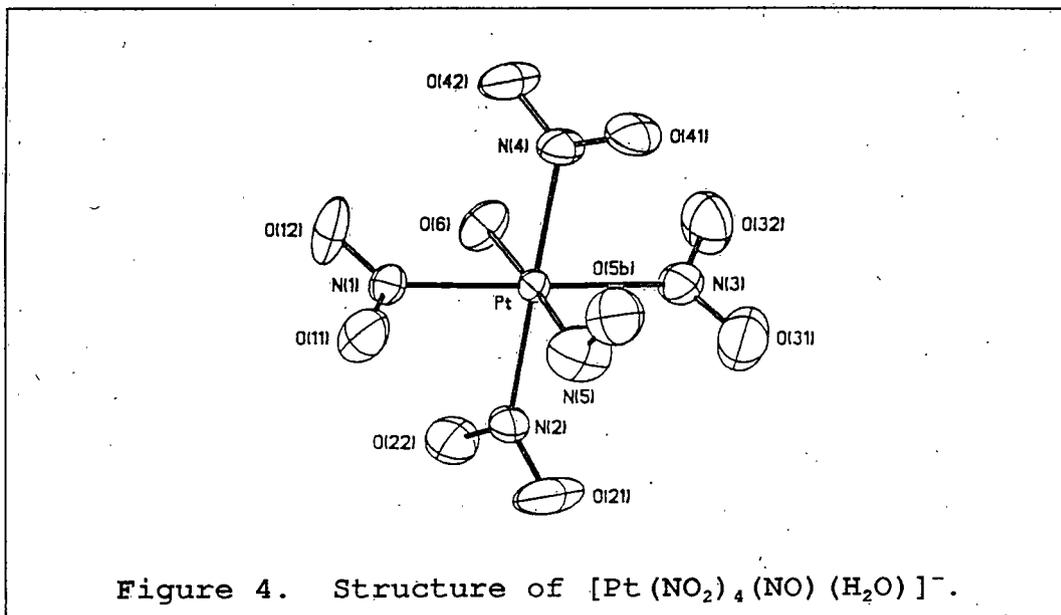


prepared with Re(40), Mo(41)(42), Rh(43), Ir(44), Ru(45), and Os(46).

In preparing this compound a series of dramatic color changes are observed; the initial solution of  $\text{K}_2\text{Pt}(\text{NO}_2)_4$  in concentrated acid turns immediately a deep blue; as the reaction proceeds, the color changes slowly over two to three hours to green, then yellow, precipitating the yellow dimer. Brown gas is evolved throughout this sequence.

These colored compounds indicated that several intermediates must be in solution; four of these have been identified and their structure determined by X-ray analysis(47)(48). The first two compounds, blue and green, are mononuclear, containing bent nitrosyl and

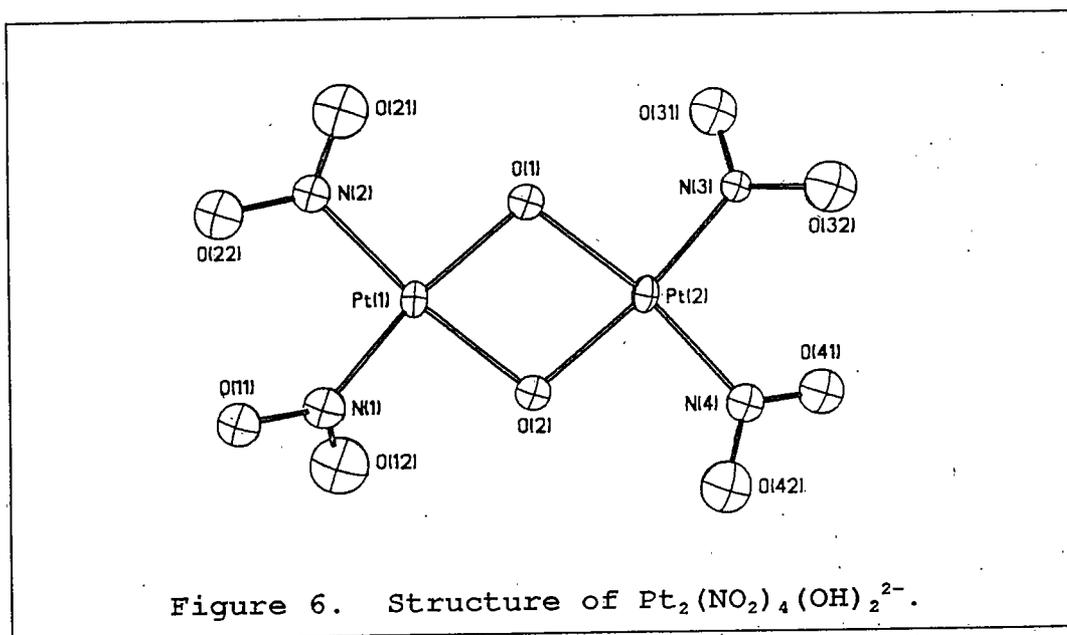
nitrite groups coordinated to the platinum atom (Figures 4 and 5). Note that in both cases the original Platinum(II) was oxidized to platinum(IV);



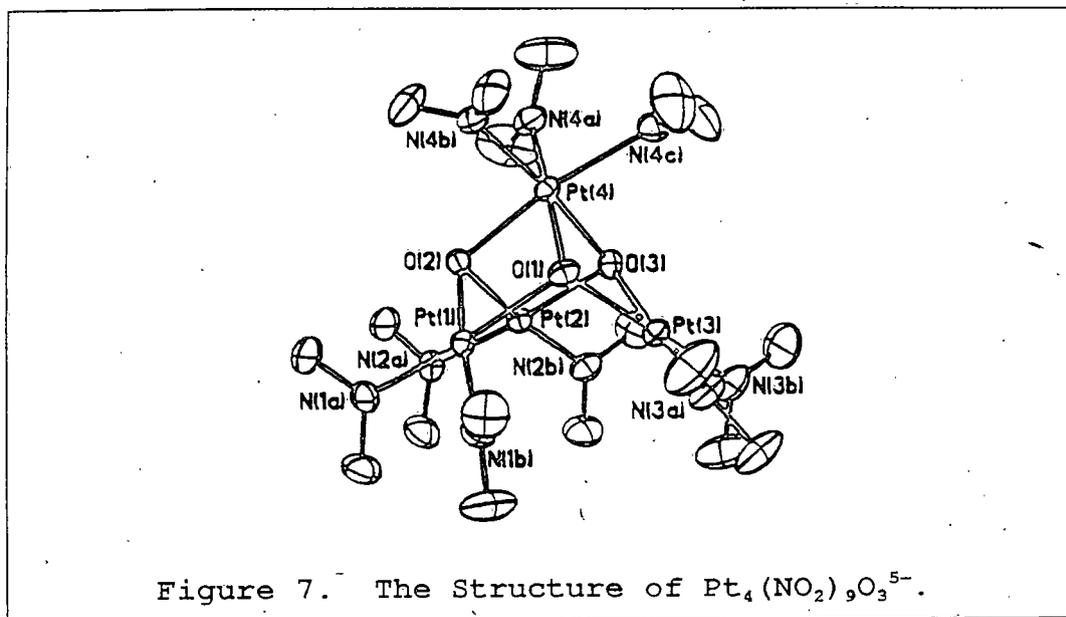
also note that for the first species,  $[\text{Pt}(\text{NO}_2)_4(\text{NO})(\text{H}_2\text{O})]^-$ ,

four nitrites and a nitrosyl are coordinated, yet the original complex began with only four nitrogen ligands ( $\text{Pt}(\text{NO}_2)_4^{2-}$ ). The extra nitrogen group must have come from another  $\text{Pt}(\text{NO}_2)_4^{2-}$  molecule, leaving at least one other compound in solution, containing at most three nitrogen ligands. The second compound,  $[\text{PtCl}_3(\text{NO}_2)_2(\text{NO})]^{2-}$ , contains contaminating chloride as a result of insufficient recrystallization of the  $\text{K}_2\text{Pt}(\text{NO}_2)_4$ , and a coordinated bent nitrosyl. These compounds represent only the second and third reported bent nitrosyl complexes of platinum(IV).

The remaining two compounds were prepared in dilute sulfuric acid later neutralized with  $\text{Na}_2\text{CO}_3$ ; these compounds are yellow, multinuclear complexes containing coordinated nitrite (Figures 6 and 7). The first



compound contains platinum(II), while the second is a



mixture of platinum(II) and platinum(IV).

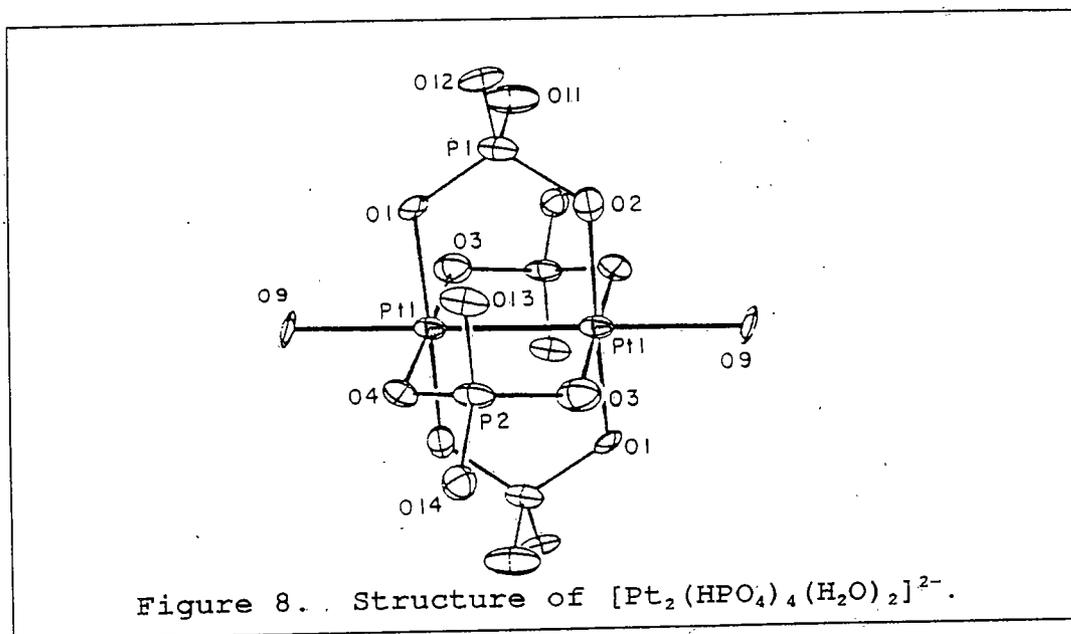
It is important to realize that these four compounds could be intermediates in the formation of  $\text{Pt}_2(\text{SO}_4)_4^{2-}$ ; all contain coordinated nitrite or nitrosyl, and three of the complexes demonstrate the oxidation of the platinum(II) to platinum(IV) preceding the formation of the platinum(III) dimer. In this paper(48) it is suggested that perhaps, since platinum(II) and platinum(IV) are present in the solution, the final platinum(III) product is formed as a result of reaction of two such species, in a mechanism like the reverse of disproportionation. Much of the focus of this thesis will deal with determining the validity of this suggestion (Chapter (III)).

The NMR analysis of the sulfate dimer and its axially substituted derivatives was first conducted by Appleton/Hall(49) (50). Reported are the

resonances for the lithium salts of the sulfate dimer and phosphate (to be discussed in more detail below) dimer, as well as a variety of compounds axially substituted with  $\text{OH}^-$ ,  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{SCN}^-$ ,  $\text{NO}_2^-$ , DMSO,  $\text{NH}_3$ , and  $\text{CN}^-$ . (The lithium salts were used because of the low solubility of the potassium salts.) The  $^{195}\text{Pt}$  NMR chemical shifts for these compounds range from 1216ppm for axially coordinated water and  $\text{SCN}^-$ , to 2049ppm for the dihydroxo-complex (all platinum NMR resonances reported are relative to the  $\text{PtCl}_6^{2-}$ , with positive resonances to lower shielding); the  $^1\text{J}$  and  $^2\text{J}$  coupling constants were also reported for platinum to carbon, platinum to nitrogen, and platinum to platinum.

### Phosphate Ligands

The first report of the phosphate analogue of the sulfate dimer was in 1980 by the same Russian group who did the first work on the sulfate dimer(51); this compound was prepared in the same way as for the sulfate, with the exception that  $\text{cis-Pt}(\text{NH}_3)_2(\text{NO}_2)_2$  was reacted with the acid. The X-ray structure was determined(38) (Figure 8), and found to be comparable to that for the sulfate dimer; the molecule maintains  $\text{C}_{4h}$  symmetry, with the phosphorus atoms slightly out of the O-Pt-Pt-O plane. The Pt-Pt distance is 2.486Å, statistically different from the 2.461Å in the sulfate dimer, but was not



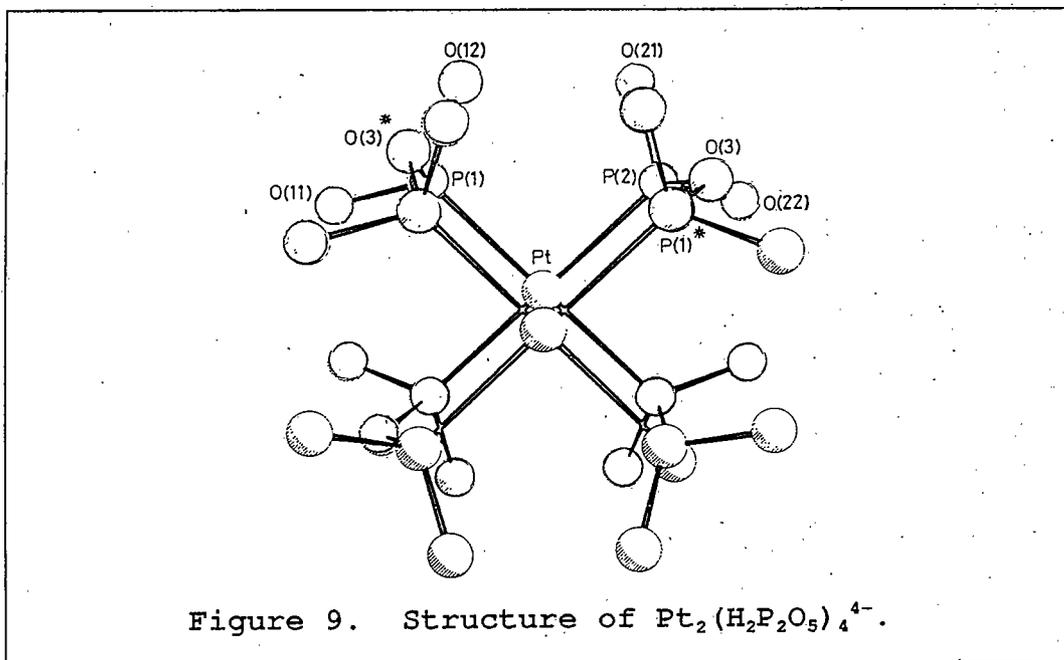
believed to reflect any significance chemically. Several axially substituted derivatives were reported with structures similar to those reported for the sulfate dimer (52). Analogous compounds have been prepared with Rh (53) and Re (54).

As for  $\text{Pt}_2(\text{SO}_4)_4^{2-}$ , the NMR spectra for the phosphate dimer and its axial derivatives ( $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{SCN}^-$ ,  $\text{NO}_2^-$ ,  $\text{CN}^-$ ,  $\text{DMSO}$ , and  $\text{NH}_3$ ) were reported by Appleton/Hall (49), (50). The  $^{195}\text{Pt}$  NMR chemical shifts of these species cover a similar range as for the sulfate complexes, from 1256 ppm for the  $\text{SCN}^-/\text{H}_2\text{O}$  compound to 1987 ppm for the  $\text{NO}_2^-/\text{H}_2\text{O}$ .

#### Pyrophosphite Ligands

The first report of the reaction of  $\text{K}_2\text{PtCl}_4$  with phosphorous acid in 1955 (55) yielded a yellow solution and platinum metal upon addition of sodium

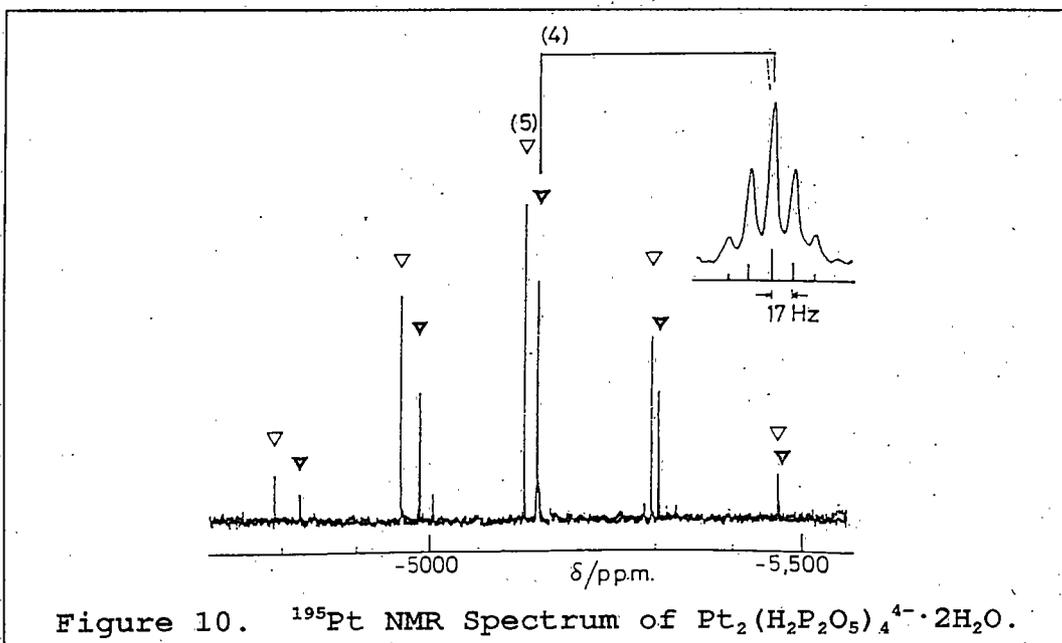
carbonate; these results were explained by Troitskaya(56) six years later: the yellow solution was due to unreacted  $\text{PtCl}_4^{2-}$ , and the platinum metal was generated by reduction by the added carbonate. The product,  $[\text{Pt}\{\text{P}(\text{OH})_2\text{O}\}_2\{\text{P}(\text{OH})_3\}_2]$ , was in fact determined to be contained in the colorless solution obtained by heating  $\text{PtCl}_4^{2-}$  with  $\text{H}_3\text{PO}_3$  in water. This work was repeated in 1977(57), with the synthesis of new mixed platinum/copper complexes bound by  $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$  (dppe) ligands, as well as the report of a side product of the original Troitskaya compound; this compound "showed an intense green emission on irradiation with UV light". A preparation in better yield with a phosphorous acid melt (instead of aqueous solution) is suggested, but the properties of the compound are reported to be identical to those of the Troitskaya compound. The synthesis has more recently been reported to be improved by evaporating aqueous solutions under inert atmosphere, using barium as the counter-ion, starting with  $\text{Na}_2\text{PtCl}_4$ , or starting with  $\text{Pt}(\text{NH}_3)_2\text{Cl}_2$ (58). The structure of this luminescent compound was reported three years later(59), and is illustrated in Figure 9; it turns out not to be mononuclear as earlier reported, but binuclear, as the intense luminescence is now believed to suggest (60), (61), (62), (63). Note the same basic construction as the sulfate and phosphate platinum(III)



dimers, with bridging pyrophosphite ligands generated by dehydration of the phosphorous acid (axially coordinated water are omitted). The Pt-Pt bond distance is 2.925Å, longer than the distance in the platinum(III) dimers, and indicates strong interaction between the two metal atoms but no bond (though it has been suggested that the bond distance might be more dependent upon the size of the bridging bite than the metal-metal interaction(64).)

The  $^{195}\text{Pt}$  NMR spectrum(59) shows a pentet of pentets (Figure 10); each platinum is coupled to the four equivalently bound phosphorus atoms, as well as to the four equivalent phosphorus atoms on the adjacent platinum atom ( $^3\text{J}$  coupled).

Many derivatives of this complex have been prepared by replacement of the axially coordinated water with



other ligands: double substitution (of the form  $\text{Pt}_2(\text{H}_2\text{P}_2\text{O}_5)_4\text{X}_2^{4-}$ ) by  $\text{Cl}^-$  and  $\text{CH}_3\text{I}$  (65);  $\text{Br}^-$  and  $\text{I}^-$  (66) (67);  $\text{NO}_2^-$ ,  $\text{SCN}^-$ , and imidazolyl (56) (68) (69), and mixed substitution of the form  $\text{Pt}_2(\text{H}_2\text{P}_2\text{O}_5)_4\text{XY}^{4-}$ ,  $\text{X}=\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ ;  $\text{Y}=\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ ,  $\text{CN}^-$ ,  $\text{NO}_2^-$  (56) (66) (70). These compounds form easily by chemical or electrical oxidation by the incoming ligand, and the ease with which they form and their stability is attributed to an increase in the bond order from zero to one between the platinum atoms (the Pt-Pt distances in these compounds are at least  $0.343\text{\AA}$  shorter than for the parent compound.)

Among the most interesting of the derivatives are those involving a single substitution of an axial water by halide ion ( $\text{Pt}_2(\text{H}_2\text{P}_2\text{O}_5)_4\text{X}^{4-}$ ) (61) (71) (72); these

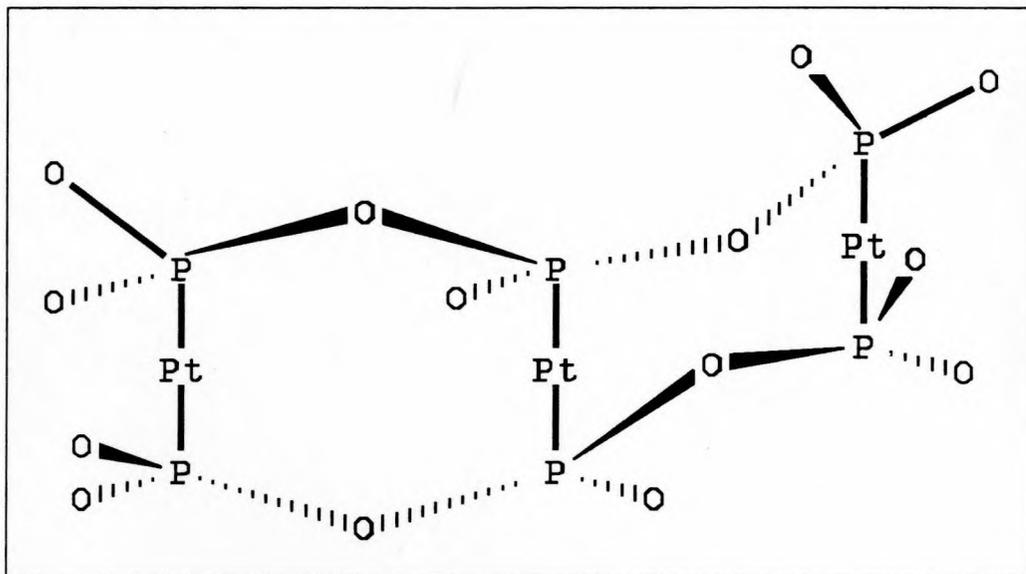
compounds do not maintain the remaining coordinated water, but instead lose it to form golden metallic products with infinite chains of ...-Pt-Pt-X-Pt-Pt-X-Pt-... linkages. These chains are made up of alternating Pt(II)-Pt(III) centers, and behave as semiconductors.

The NMR spectra of the derivatives are very similar to those of the parent compound for identical substituents, but become very complicated when the substituents differ, due to all the extra coupling to the now different phosphorus and platinum atoms.

The trimeric compound proposed by Roundhill is worthy of more detailed consideration here, for it is a higher oligomer of this system. The green dimer ( $\text{Pt}_2(\text{H}_2\text{P}_2\text{O}_5)_4^{4-}$ ) is formed by heating a solution of  $\text{PtCl}_4^{2-}$  with  $\text{H}_3\text{PO}_3$  to dryness at  $100^\circ\text{C}$ ; Roundhill reports that if this condensation (and concomitant dehydration of the phosphorus ligand) is conducted at  $170^\circ\text{C}$ , a new species is formed as a dark green powder, with intense red luminescence at room temperature; this compound allegedly contains bridging triphosphite ( $\text{O}_2\text{POP}(\text{O})\text{OPO}_2^{3-}$ ), with a trinuclear platinum core. The  $^{31}\text{P}$  NMR spectrum of this complex is reported to have broad resonances, and fall at 62.1ppm with platinum satellites ( $^1J=3250\text{Hz}$ ). In addition to this compound, another compound is formed at yet higher temperatures; this compound has a 'vermillion red' color, and is insoluble in water and organic

solvents.

This 'vermillion red' compound appears to be the same compound studied by us for several years, and the results of that work are reported in Chapter III. Roundhill's assignment of the dark green compound, however, to a trimer with four bridging triphosphite ligands is flawed; it is not possible to get four triphosphite ligands around a linear three metal center! The triphosphite ligand is bent, just as propane is bent (see below); while a ligand can bridge across the



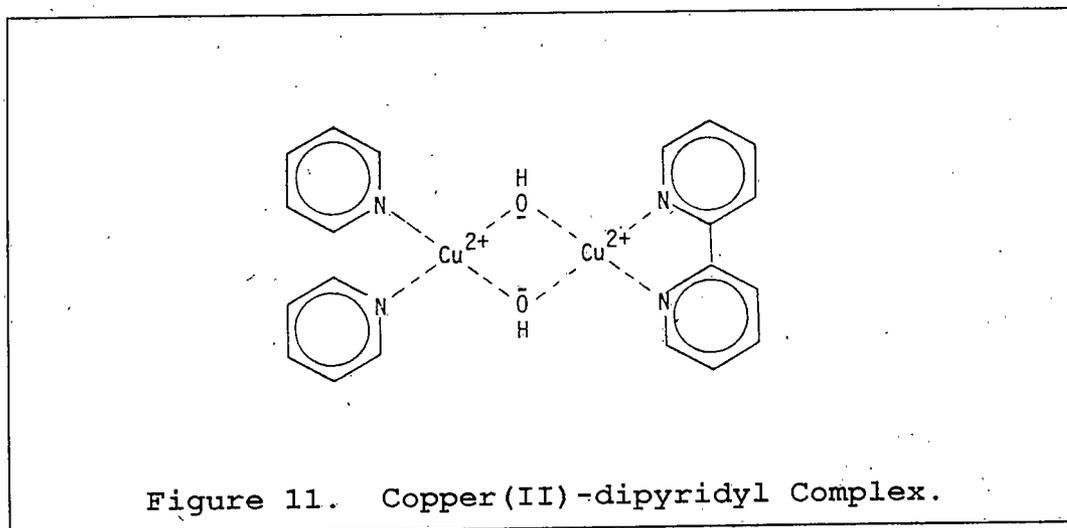
top, and another across the bottom of a linear trimer, it is not possible to coordinate another ligand across the chain, as these ligands would deform the linear arrangement of metal centers, disrupting the coordination across the top and bottom. Thus, while the complex no doubt has multiple platinum centers, they cannot be arranged in a linear fashion. Further, Roundhill offers

no support for the premise that triphosphite is present; the  $^{31}\text{P}$  NMR spectrum should show two distinctly different kinds of phosphorus atoms, doubtless coupled to each other as well as to the two different kinds of platinum atoms. The  $^{195}\text{Pt}$  NMR spectrum should show two different kinds of platinum atoms (which it does), but for the proposed structure to be correct they must have a one to two ratio: one central platinum atom to two terminal platinum atoms. While the peaks are reported to be of unequal intensity, the vital information of their actual ratios is absent. Similarly, no IR information is given, which would indicate the possible presence of triphosphite.

#### **Polymerization with Aquo/Hydroxo Ligands**

The first thorough study of dimerization of metal complexes was by equilibrium measurements on chelate compounds; Gustafson and Martell(73) reported in 1959 on the dimerization of 1:1 copper(II) dipyridyl and o-phenanthroline complexes. Their studies demonstrated that as the pH of the solution approached neutrality, hydroxo-bridges form to give a structure as in Figure 11. They also reported that at high pH, the dimeric species decomposed to yield mononuclear complexes.

Since that time the polymerization of many other metals under these conditions has been studied.



Oxidation of the hexaaquochromium(II) ion induces polymerization with hydroxide bridges to form dimers (at acidic pH), and trimers, tetramers, pentamers, and hexamers as the pH increases (74). Complexes containing three hydroxide bridges have been reported (75), as well as the isomerization of  $\text{Cr}_4(\text{OH})_7^{5+}$  (produced by reaction of  $\text{Cr}_4(\text{OH})_6^{6+}$  with base) to  $\text{Cr}_4(\mu\text{-O})(\text{OH})_5^{5+}$  (76).

Oxidation of cobalt is reported to yield not only two and three centered species upon raising pH, but a tetrameric complex  $([\text{Co}\{\mu\text{-OH}\}_2\text{Co}(\text{NH}_3)_4\}_3](\text{SO}_4)_3 \cdot 4\text{H}_2\text{O})$  as well (77), and complexes containing three hydroxide bridges (78), (79). Rhodium forms dimeric clusters with two and three bridges (80), as does iridium (81), which also forms dimers from  $\text{Ir}(\text{H}_2\text{O})_6^{3+}$  in  $2\text{M HClO}_4$  (82).

Perhaps the richest such polymerization occurs with

iron, manganese, and vanadium. Iron is known to form oligomers with as many as twelve metal atoms(83), manganese forms many dimers and trimers(84), as does vanadium in vanadates;  $OV(IV)$  reacts to form 1:1 oxovanadium chelates of salicylic acid, sulfosalicylic acid, 3,5-disulfopyrocatechol (tiron), and 5-sulfo-8-hydroxyquinoline, all of which dimerize at mildly acidic pH(85). These dimers are reported to be 'intermediates in the formation of extensively hydrolyzed and polymerized polynuclear vanadyl species.'

Of particular interest to this work is the nature and facility of such dimerization reaction with platinum. Most recently the focus of such studies has dealt with the formation of polynuclear complexes of *cis*-platin and its analogues; at near neutral pH these compounds readily dimerize to form complexes(86)(87)(88)(89)(90)(91) as in Figure 12. Such compounds are of interest, as physiological pH is very near neutral, and the active forms of the anti-cancer drug *cis*-platin are no doubt similar to these compounds.

In the early sixties the dimerization and polymerization of platinum(III) species (discussed earlier) and platinum(IV) became of interest; an early review of this work was presented by Sidgwick(92), who mentions on page 1621, for example, that the reported compound  $PtO_2 \cdot 4H_2O$  is probably polymerized  $H_2Pt(OH)_6$ .



less acidic media.

The work described in the remainder of this paper deals with the synthesis, identification, and study of the mechanism of formation of a group of multinuclear platinum compounds related to the compounds described in this introduction. First will be the synthesis and characterization of a polymeric compound related to the pyrophosphite dimers; followed by experiments which shed light on the nature of platinum(IV) in acidic media, leading to a potential mechanism for the formation of the platinum(III) dimers which can be used to form new dimeric species.

## CHAPTER II

## EXPERIMENTAL

This chapter describes the experimental conditions and parameters under which the data to be described were obtained.

**Nuclear Magnetic Resonance**

Most of the spectra discussed in this work were collected on a Bruker WM 250 NMR Spectrometer using a tuneable 10mm broadband probe; the remainder collected on a Bruker AM 500 instrument will be noted as such. All experiments were conducted with samples of platinum concentration in the 20-50 mM range.

Table 1 lists typical operating parameters for  $^{195}\text{Pt}$  and  $^{31}\text{P}$  data collections; the number of scans usually ranged from 16,000 to 40,000, occasionally as many as 75,000 for platinum, and 1500 to 3000 for phosphorus.

Samples were run with  $\text{D}_2\text{O}$  as a lock standard either in solution, or as an external standard; experiments run in DMSO used  $\text{D}_6$ -DMSO as lock standard.

Spectrometer Frequency	53.518MHz	101.250MHz
Synthesizer Frequency	98.04- 98.34MHz	74.47MHz
Observation Frequency	868Hz	70,845Hz
Spectrum Size	1-2K	8K
Spectral Width	50,000Hz	20,000Hz
Receiver Delay	0 sec	1.5sec
Aquisition Time	.01-.02sec	.203sec
Receiver Gain	800	100
Pulse Width	30 usec	18 usec
Line Broadening	25Hz	3Hz

### Infrared

Infrared spectra were collected on a Nicolet 5DX as KBr or Nujol mulls.

### UV-Vis

UV-Vis spectra were collected on a Cary-14 in dilute aqueous solution, or as a KBr mull.

### X-Ray Photoelectron Spectroscopy

XPS spectra were collected on a Leybold-Hereaus hemispherical EA11 energy analyzer, using a Mg K<sub>α</sub> X-ray source in a UHV system; this source emits electrons with an energy of 1253.6 eV. A sample of a few milligrams was

physically rolled into the surface of a piece of indium foil, and introduced into the analysis chamber. Surface charging effects were compensated for by monitoring and adjusting the chemical shifts of the indium and carbon absorbances.

### Fluorometry

Fluorescence data were collected with a Spex Fluorolog 2 Model F211; a 1.2mm slit was used in the excitation monochromator (2.25nm bandpass), and a 0.5mm slit in the emission monochromator (1.8nm bandpass). Data were corrected to detector response, and front face collected.

### X-Ray Crystallography

Intensity data were collected on a Nicolet R3mE four circle diffractometer. Crystals were mounted on a glass fiber for reflection collection, and between 18 and 23 centered reflections were used to determine the unit cell dimensions by least squares refinement (radiation source of graphite-monochromatized Mo  $K_{\alpha}$ ). Platinum positions were determined by Patterson synthesis, and remaining atoms by difference synthesis.

## CHAPTER III

## RESULTS/DISCUSSION

We will now consider the reactions which lead to some new multinuclear platinum clusters in the systems discussed in the Introduction. First will be the synthesis and characterization of a polymeric species which is a higher oligomer of the pyrophosphite dimer  $\text{Pt}_2(\text{H}_2\text{P}_2\text{O}_5)_4^{2-}$  (described under the section titled 'Red Compound'); this compound probably contains molecules of somewhat varying length. A structure will first be proposed based upon elemental analysis data and other experimental data in support of this structure will follow. Second (beginning with the section titled 'The Concept of Reverse Disproportionation') are detailed the results of experiments seeking to form the sulfato- and phosphato-  $\text{Pt}_2\text{X}_4^{2-}$  dimers by a systematic, reasoned approach-- the reverse of disproportionation; in the process of these reverse disproportionation reactions were also studied the nature of the polymerization of platinum(IV) in mineral acids, and the formation of many new platinum(II) and platinum(IV) mononuclear complexes in strong organic acids.

**Red Compound**SynthesisPotassium Salt

$K_2PtCl_4$  (381.6 mg. 0.930 mmoles) and  $H_3PO_3$  (2648.7 mg, 32.3 mmoles) were dissolved in deionized water and the resulting solution refluxed in an oil bath until colorless. This solution was then transferred to a petri dish and heated to near dryness on a hot plate (surface temperature of which was 220-240 °C.) As the solution approached dryness the green color of the  $Pt_2(POP)_4^{4-}$  ion began to appear. Seven minutes from the first appearance of this color (at which point the mixture was a darker green oil) the petri dish was removed from the hot plate and allowed to cool to room temperature; during these seven minutes the syrup was swirled occasionally. As it cooled, the color of the mixture changed to dark red; this dark red mixture had an intense red luminescence at room temperature (the luminescence was more intense at room temperature than at elevated temperatures.) The oil was washed four times with five to ten mL of methanol, and then acetone, to remove excess  $H_3PO_3$ , and dried at room temperature under vacuum to yield a red solid.

If the condensed oil was heated longer than seven minutes at this temperature it formed a dark purple compound, which did not change color as it cooled from

the high temperatures at which it formed, and has no luminescence.

The synthesis is reversible: addition of water to the dried solid produced a deep red solution of the red compound, which luminesced orange; as time progressed the solution became green with green luminescence, and finally colorless; if the solution was heated at near 100 °C this transformation took only a minute or two (the same behavior was observed for the dark purple compound, which also formed the dark red solution in water.) The orange luminescence observed as the complex decomposed seemed to arise from a mixture of red and green luminescence (red from the complex, and green from  $\text{Pt}_2(\text{POP})_4^{4-}$ ). This combination of red and green emission, appearing orange, differs from a combination of red and green reflected light, which would appear brown(97).

Occasionally a light blue solution resulted (which did not change with heating), and produced light blue solids; these solids were insoluble in acetone and methanol, but dissolved in water to produce red/orange to yellow solutions with green luminescence. These solutions turned blue after about three hours. The blue solids obtained turned red/orange upon drawing air through them for drying; this suggested that the blue compounds were reduced platinum species, for they underwent oxidation by air to convert to the red com-

pound.

Also occasionally a yellow solution was obtained instead of red, which remained yellow even if heated or condensed at 200 °C. Yellow solids isolated from these solutions were soluble in methanol, acetone, and slightly soluble in water; solutions in methanol to which were added diethyl ether to try to precipitate the solid turned lavender.

In two cases, after heating at 210-250°C for eight minutes, an orange/red oil was obtained which upon addition of water yielded an orange solution whose color did not change even upon heating to dryness. The orange solid obtained had a green luminescence. Reheating with more water caused no change. After storage at room temperature for five days, the solution was brown/black; heating this solution to a thick oil at approximately 100 °C for 15 minutes produced sparks and fire, leaving black solid in the regions of the petri dish where the fire occurred.

This red polymer was also prepared, with more difficulty, by heating the solution of  $K_2PtCl_4$  and  $H_3PO_3$  in water to dryness in an oven. A solution in six mL of water was put in an oven at 110 °C; after 100 minutes only colorless crystals of  $H_3PO_3$  were observed. A further 80 minutes at this temperature still did not produce the red compound, and the temperature was raised



















































































































































































































































































