



Synthesis, characterization, and mechanistic studies on a group of platinum complexes using ^{195}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 K_2PtCl_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}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 $\text{P}(\text{OH})_3$ 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 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 $(\text{CH}_3)_4\text{NI}$ 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, 16.3354Å) and $\text{Pt}_2(\text{POP})_4\text{Br}_2$ (cell dimensions 15.2880, 15.2921, 11.6217Å). Results of many reactions of the polymer with SCBT, CNT, CH_3COOH , HN_3 , H_2S_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 H_2S_4 , H_3P_4 , HC_4O_4 , HN_3 , and $\text{CF}_3\text{SO}_3\text{H}$ are reported. Elemental analysis of the polymeric solids formed in H_2S_4 indicates 3-5 platinum atoms per anion and 12:1 for the H_3P_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_3P_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 $\text{Pt}_2(\text{S}_4)_4^{2-}$ 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}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
¹⁹⁵PT NUCLEAR MAGNETIC RESONANCE**

by

Danny Richard Bedgood, Jr.

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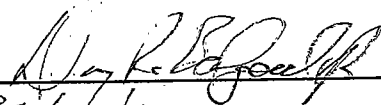
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ABSTRACT

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

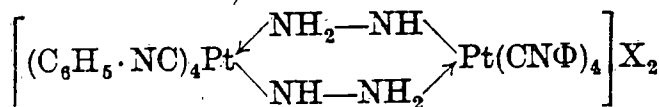


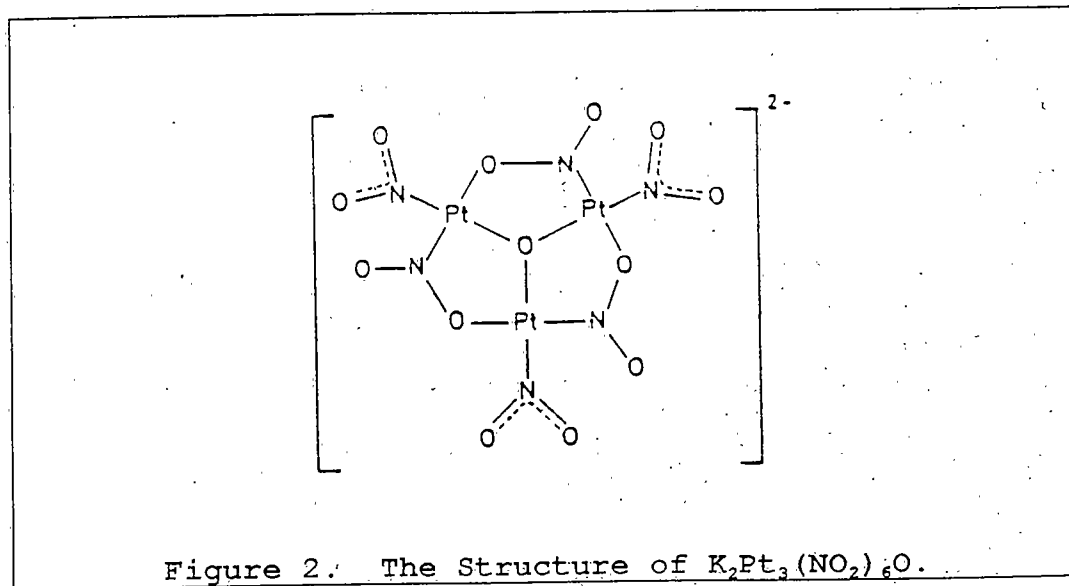
Figure 1. The Structure of
 $[(\text{C}_6\text{H}_5\text{NC})_4\text{Pt}(\text{u-NH}_2\text{NH})_2\text{Pt}(\text{CNC}_6\text{H}_5)_4]\text{X}_2$.

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

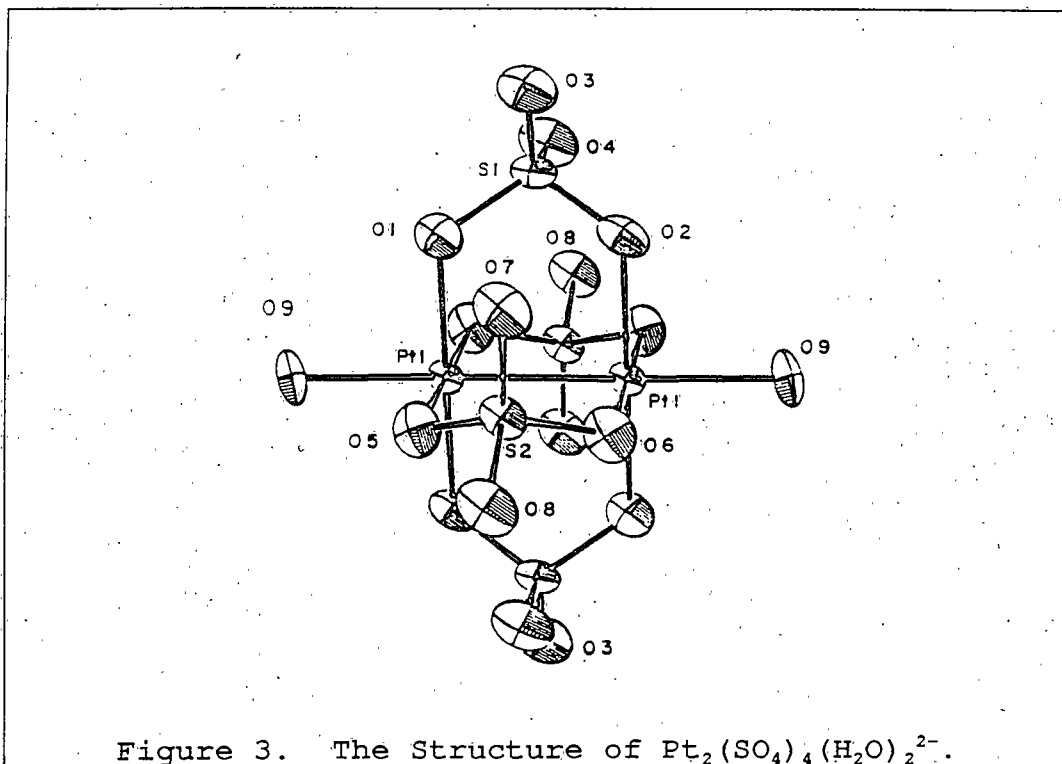
As mentioned above, Blondel reported that the reaction of PtO_2 with concentrated sulfuric acid and oxalic acid reduction resulted in a compound that analyzed as $\text{K}[\text{Pt}(\text{SO}_4)_2] \cdot \text{H}_2\text{O}$ (4). This was a modification of the reactions reported by Vezes in 1893 (27) (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 H_2SO_4 to yield a compound proposed to contain platinum(III); a compound similar to this was reported from the reaction of 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 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\AA , indicating strong interaction between the metal atoms designated as a single bond. Several analogous compounds have now been

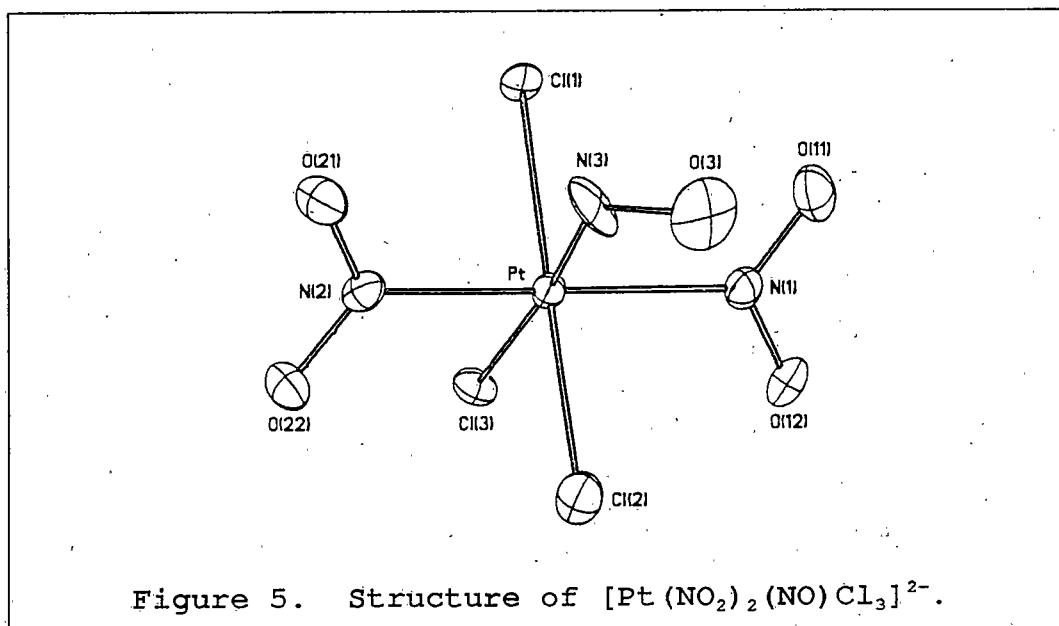
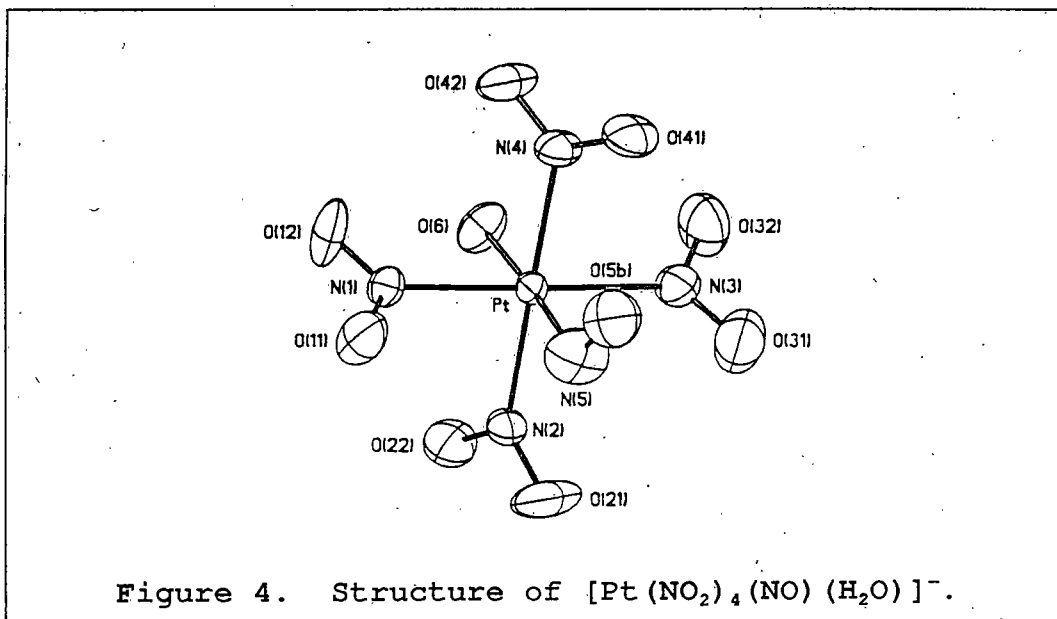


prepared with Re(40), Mo(41)(42), Rh(43), Ir(44), Ru(45), and Os(46).

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

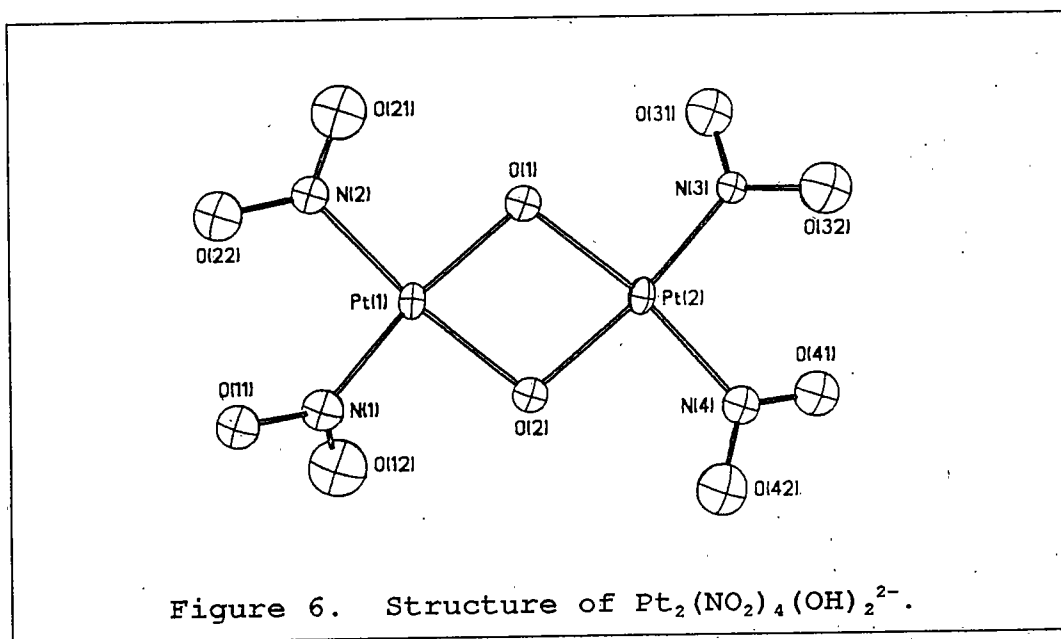
nitrite groups coordinated to the platinum atom (Figures 4 and 5). Note that in both cases the original Platinum(II) was oxidized to platinum(IV);



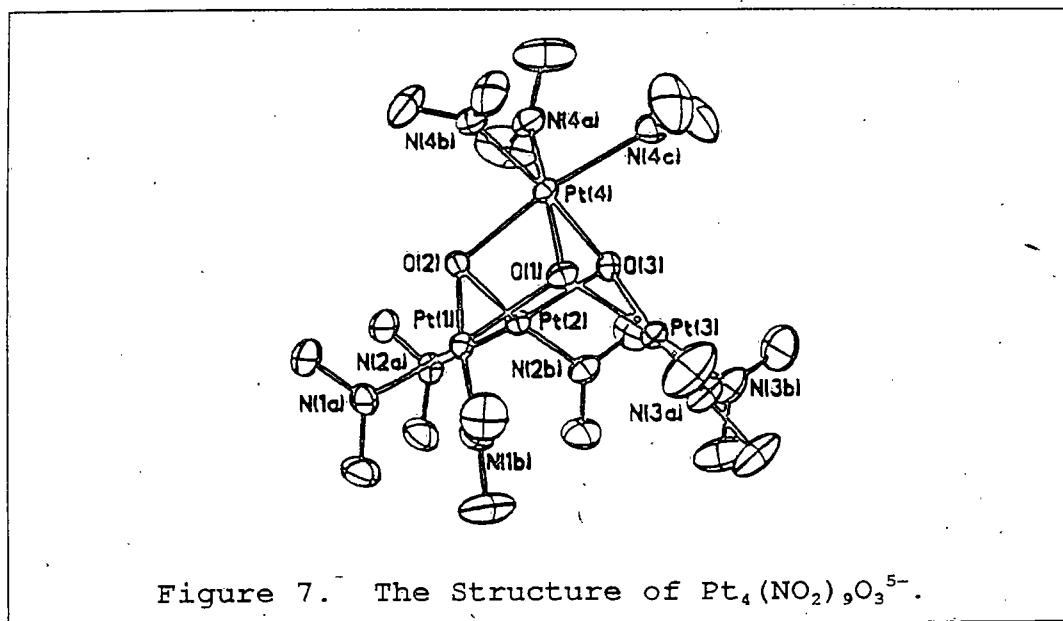
also note that for the first species, $[\text{Pt}(\text{NO}_2)_4(\text{NO})(\text{H}_2\text{O})]^-$,

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 Na_2CO_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).

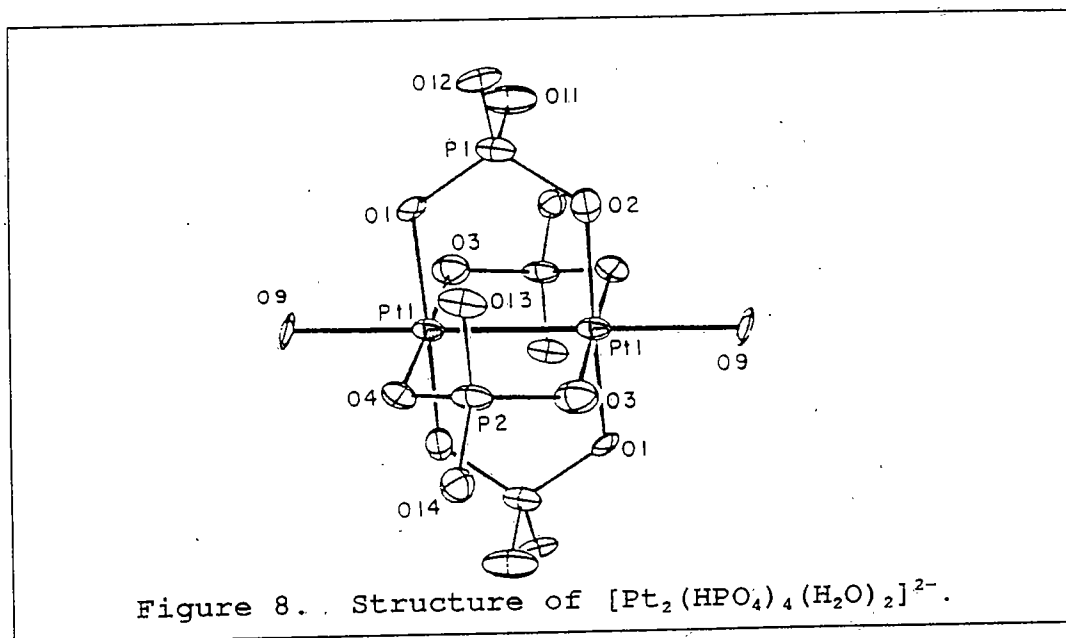
It is important to realize that these four compounds could be intermediates in the formation of $\text{Pt}_2(\text{SO}_4)_4^{2-}$; all contain coordinated nitrite or nitrosyl, and three of the complexes demonstrate the oxidation of the platinum(II) to platinum(IV) preceding the formation of the platinum(III) 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 OH^- , Cl^- , Br^- , SCN^- , NO_2^- , DMSO, NH_3 , and CN^- . (The lithium salts were used because of the low solubility of the potassium salts.) The ^{195}Pt NMR chemical shifts for these compounds range from 1216ppm for axially coordinated water and SCN^- , to 2049ppm for the dihydroxo-complex (all platinum NMR resonances reported are relative to the PtCl_6^{2-} , with positive resonances to lower shielding); the ^1J and ^2J 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 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



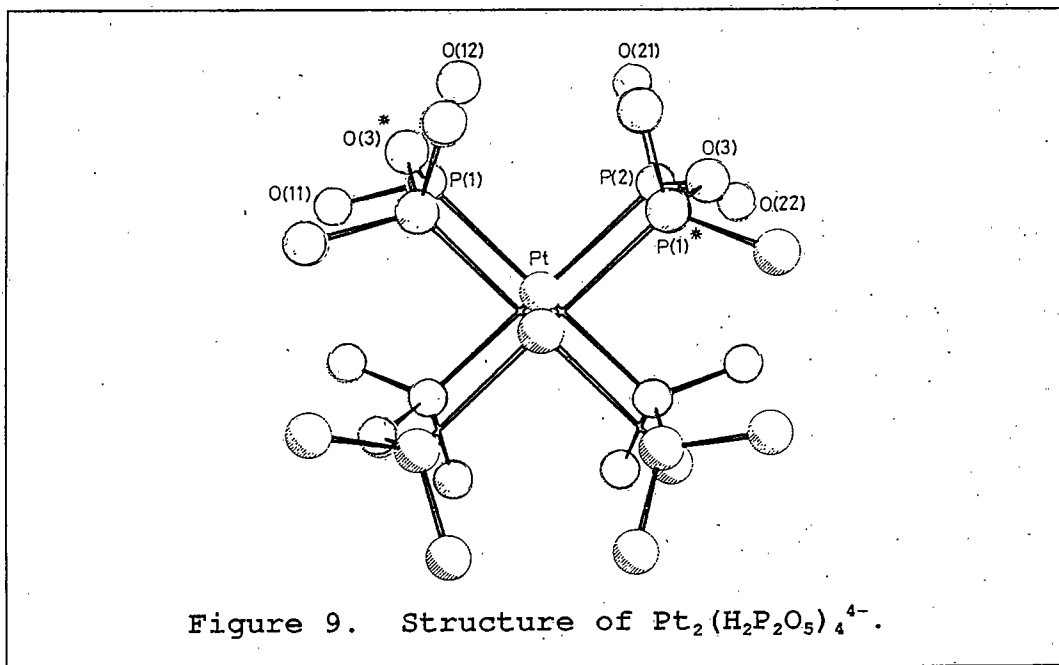
believed to reflect any significance chemically. Several axially substituted derivatives were reported with structures similar to those reported for the sulfate dimer (52). Analogous compounds have been prepared with Rh (53) and Re (54).

As for $\text{Pt}_2(\text{SO}_4)_4^{2-}$, the NMR spectra for the phosphate dimer and its axial derivatives (Cl^- , Br^- , SCN^- , NO_2^- , CN^- , DMSO , and NH_3) were reported by Appleton/Hall (49), (50). The ^{195}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 K_2PtCl_4 with phosphorous acid in 1955 (55) yielded a yellow solution and platinum metal upon addition of sodium

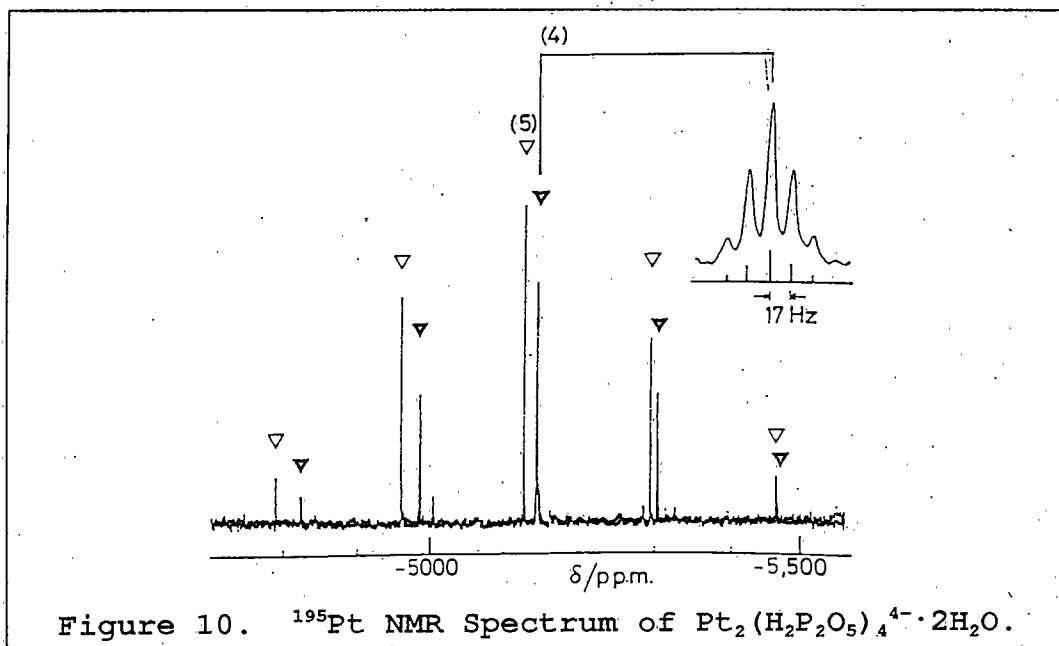
carbonate; these results were explained by Troitskaya(56) six years later: the yellow solution was due to unreacted PtCl_4^{2-} , and the platinum metal was generated by reduction by the added carbonate. The product, $[\text{Pt}\{\text{P}(\text{OH})_2\text{O}\}_2\{\text{P}(\text{OH})_3\}_2]$, was in fact determined to be contained in the colorless solution obtained by heating PtCl_4^{2-} with H_3PO_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 Na_2PtCl_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}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 (^3J 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 Cl^- and CH_3I (65); Br^- and I^- (66) (67); NO_2^- , SCN^- , and imidazolyl (56) (68) (69), and mixed substitution of the form $\text{Pt}_2(\text{H}_2\text{P}_2\text{O}_5)_4\text{XY}^{4-}$, $\text{X}=\text{Cl}^-$, Br^- , I^- ; $\text{Y}=\text{Cl}^-$, Br^- , I^- , CN^- , 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\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

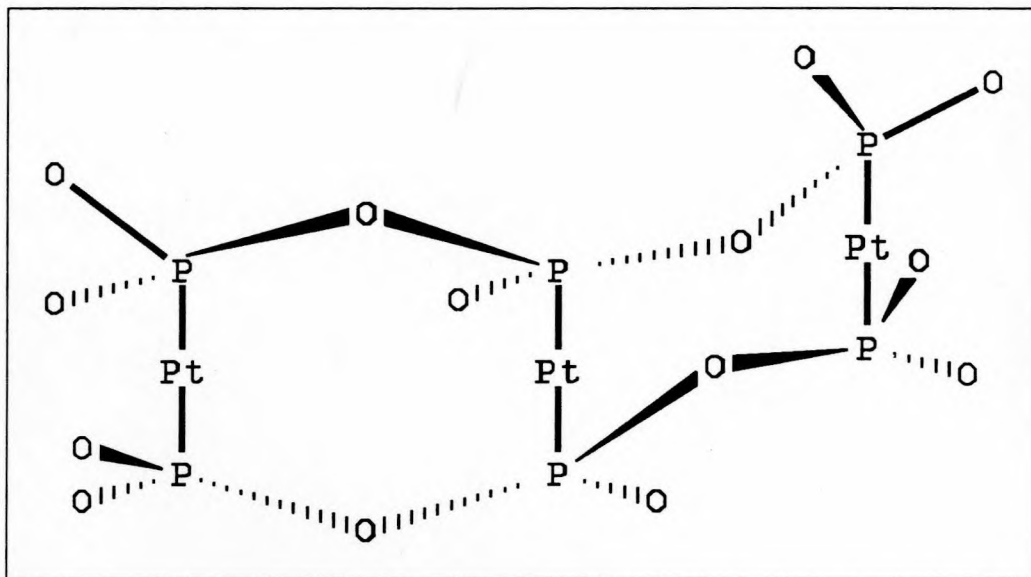
compounds do not maintain the remaining coordinated water, but instead lose it to form golden metallic products with infinite chains of ...-Pt-Pt-X-Pt-Pt-X-Pt-... linkages. These chains are made up of alternating Pt(II)-Pt(III) centers, and behave as semiconductors.

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 PtCl_4^{2-} with H_3PO_3 to dryness at 100°C ; Roundhill reports that if this condensation (and concomitant dehydration of the phosphorus ligand) is conducted at 170°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}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



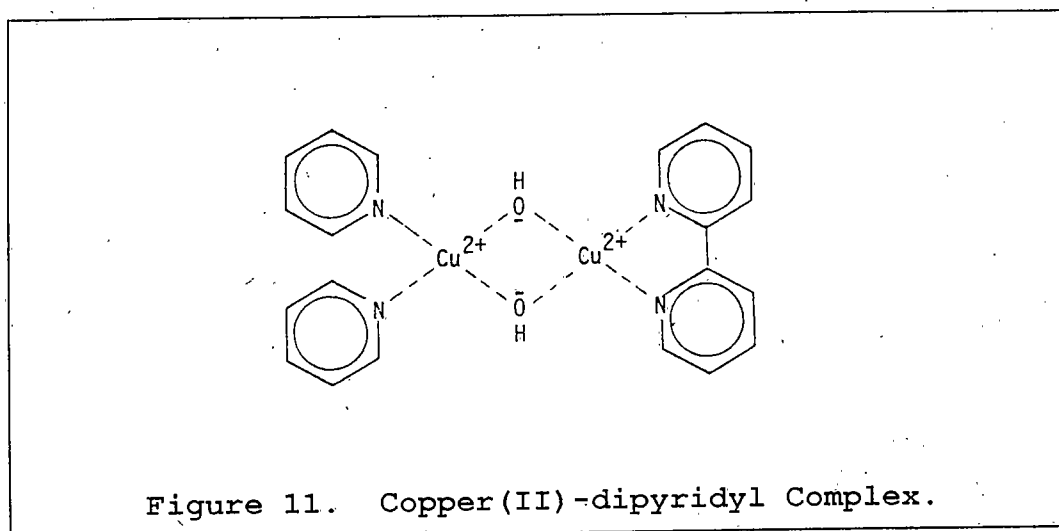
top, and another across the bottom of a linear trimer, it is not possible to coordinate another ligand across the chain, as these ligands would deform the linear arrangement of metal centers, disrupting the coordination across the top and bottom. Thus, while the complex no doubt has multiple platinum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

no support for the premise that triphosphite is present; the ^{31}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}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 2M 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 $H_2Pt(OH)_6$.

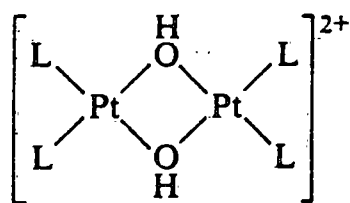


Figure 12. Hydroxo-Bridged Dimers of *cis*-Platin.

Since this time, much of the published work in the area of platinum(III) and platinum(IV) oxidation has been done by the Russians. In connection with their work on the platinum(III) sulfate and phosphate dimers, some studies of the condition of $\text{Pt}(\text{OH})_6^{2-}$ in strong acid have been reported. Hexahydroxoplatinate(IV) is reported to polymerize in perchloric and sulfuric acids (93), (94) to form cationic species (as does $\text{Pd}(\text{OH})_2$), that decompose to form monomeric complexes at high pH (>10). It was soon reported (95) that the product isolated from the solution of polymerized platinum(IV) in 25% sulfuric acid analyzed for a platinum to sulfate ratio of 4:1, supporting the earlier work indicating the platinum oligomer was cationic; experiments on the products from phosphoric acid solutions also indicated a high platinum to phosphorus ratio. This work continues, the latest paper (96) suggesting that monomeric sulfate complexes predominate in 2-5M H_2SO_4 (platinum concentration approximately 10^{-4} M), with polynuclear hydroxosulfato compounds present in

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}Pt and ^{31}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 D_2O as a lock standard either in solution, or as an external standard; experiments run in DMSO used 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_α 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_{α}). 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 CompoundSynthesisPotassium 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

to 150 °C; 140 minutes later the red solid was obtained upon allowing the mixture to cool to room temperature.

Since this polymer formed under the same dehydrating conditions as the phosphorous acid bridge in the green pyrophosphite dimer and Roundhill's compound form, attempts were made to form the red compound at lower temperatures by pumping off water to dehydrate the bridges. Beginning with the colorless solution obtained from refluxing K_2PtCl_4/H_3PO_3 in water, the solution in five mL of water was pumped overnight at room temperature over concentrated sulfuric acid; this produced no change beyond a slight loss of volume. The temperature was raised to 65 °C for 45 minutes, which produced a purple solid which luminesced orange, and a small amount of pale lavender solid with no luminescence. In a different experiment, pumping for three days at room temperature produced yellow and purple solids, all of which luminesced green. Addition of water to this mixture yielded a red solution as the brown/purple solid dissolved first, which lightened slightly as the yellow solid dissolved more slowly; the solution luminesced green. Heating this red solution to dryness produced green/purple solids. These solids redissolved in water to give a red solution, to which was added $(CH_3)_4NNO_3$ in an attempt to crystallize the species in solution; the solution turned yellow/orange upon addition of the ammonium salt, and was

put in a refrigerator. No solids of crystallographic quality were obtained.

An attempt was made to make the red compound using $K_2Pt(NO_2)_4$ as the starting material instead of K_2PtCl_4 , reasoning that the removal of chloride might expedite the formation of the complex, analogous to the formation of the platinum(III) sulfate and phosphate dimers. Refluxing the platinum nitrite species with H_3PO_3 in water for 50 minutes produced a black solution, probably due to nitrite ion reducing the platinum to platinum metal.

The potassium salt was somewhat sensitive to air and moisture, and more sensitive to light; even stored in the dark under argon, over a few months the compound decomposed to a white powder.

Sodium Salt

The sodium salt of the red complex was formed in the same manner as for the potassium salt, except using Na_2PtCl_4 as a starting material; Na_2PtCl_4 was prepared using Amberlite IR-120 C.P. ion exchange column converted to the sodium salt with NaCl.

The sodium salt behaved the same as the potassium salt, forming the dark purple compound at longer heating times; the occasional odd reactions observed for the potassium salt were not observed, but this is probably due to the fewer times the sodium salt was prepared.

The sodium salt was much more sensitive to air,

moisture, and light than the potassium salt; after a few days the solid began to turn orange, luminesce green/orange, and after two weeks the solid had turned white, even under vacuum in the dark.

Methyltriphenylphosphonium salt

The potassium salt of the red compound (155.7mg) was dissolved in two mL's of deionized water and precipitated with five mL's of a 0.1566 M aqueous solution of $(\text{CH}_3)-(\text{C}_6\text{H}_5)_3\text{PNO}_3$ (the same results were obtained for the bromide salt of the cation.) The resulting flocculent red solid was filtered from the yellow solution and washed four times with 10 mL of water, and then with acetone several times and dried with NaOH pellets in a drying pistol containing refluxing toluene. Yield was 80.0 mg, or 35% based on platinum. As the solid was washed with water, the washes changed from pale yellow to colorless; more than about four washes of the solid with water caused the washes to become pale yellow again.

The resulting red luminescent solid was very stable, maintaining its color and luminescence for months in air and light, and over a year in the dark.

Properties

Elemental Analysis

The results of elemental analysis of methyltriphenylphosphonium salts of the red complex appear in Table 2.

Several other analyses were performed on early preparations; the results below are those for the best preparations. The discrepancies between the two samples are attributed to small differences in the proportions of different sized polymers present.

Sample	% Pt	% P	% C	% H	% O*
1	23.31	19.42	29.94	3.30	23.44
2	23.65	19.74	31.22	3.44	21.95
* by difference					

The samples were also analyzed for potassium and chloride, both of which were found to be present in only trace amounts (K=0.19%, and Cl<0.4%).

Interpretation of these results led to a compound with a ratio of platinum to cation of 5:6. The multinuclearity indicated by this data was cause for excitement! Not only did the intense red luminescence indicate an interesting structure(60), but the elemental analysis supported such a conclusion. Analysis of these data was as follows:

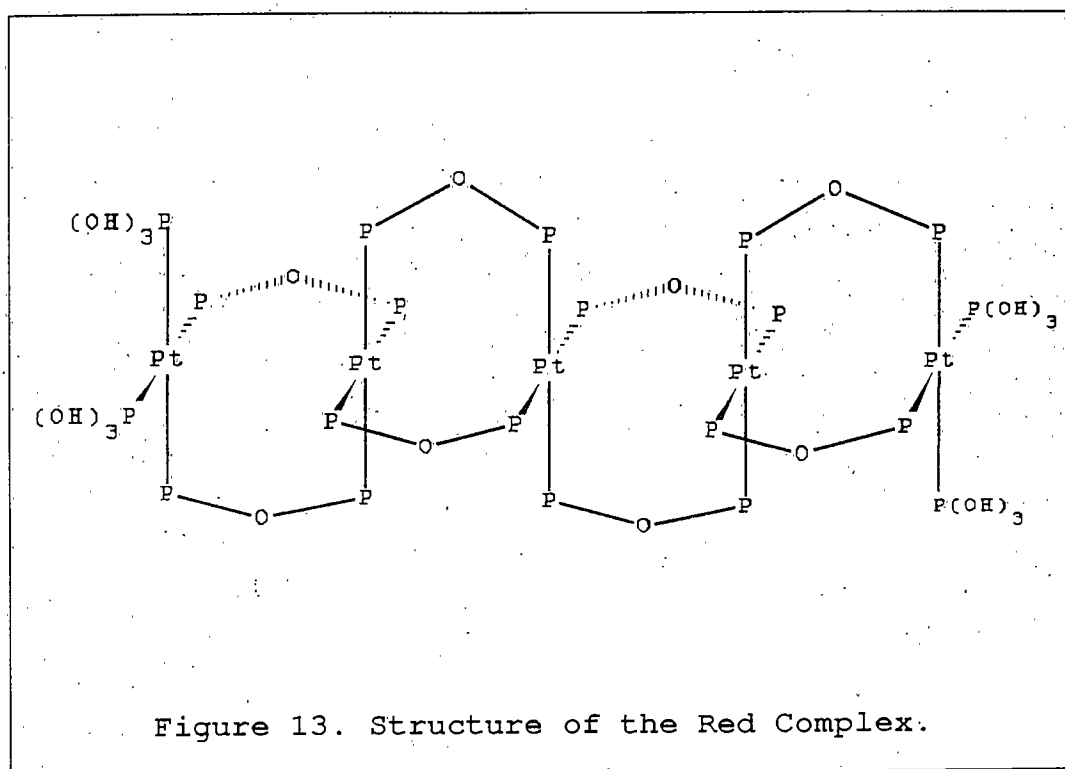
The number of cations per platinum was easily determined by the ratio of moles of carbon to moles of platinum, as the only source of carbon in the complex is due to the cation; this ratio is 1 Pt: 1.1 cations.

The phosphorus present must arise from two sources:

the coordinated ligand and the cation. Knowing the number of cations is 1.1, the amount of phosphorus due to the cation was subtracted from the total moles of phosphorus to determine the number of moles of coordinated phosphorus. In this way the ratio of coordinated phosphorus to platinum was found to be 4:1, as might be expected from the similarity of the synthesis of the red complex and $\text{Pt}_2(\text{POP})_4^{4-}$.

The amount of oxygen present (by difference) gave an oxygen to phosphorus ratio of between 2.7 and 2.9:1; this ratio was higher than the 2.5:1 we would find should all the coordinated phosphorus be present as pyrophosphite, indicating the ligand cannot be triphosphite or another more highly dehydrated form of pyrophosphite (the oxygen to phosphorus ratio drops below 2.5:1 for each successive dehydration beyond pyrophosphite). Some of the phosphorus bound to the platinum must have been present as phosphorous acid, which has one more oxygen per phosphorus, (a P:O ratio of 1:3). The coordination of phosphorous acid also reduced the charge on the complex; if all phosphorus were bound as pyrophosphite, the six cations per five platinum atoms would leave a highly negatively charged anion. As phosphorous acid can coordinate as a neutral ligand under these conditions (57), (98), (99), (100), the apparent discrepancy of charge of the seemingly low number of cations was explained.

The proposed formula for the red complex based upon these elemental data was $(\text{CH}_3(\text{C}_6\text{H}_5)_3\text{P})_6[\text{Pt}_5(\text{P}_2\text{O}_5\text{H}_2)_8(\text{P}(\text{OH})_3)_4] \cdot 4\text{H}_2\text{O}$, with a structure containing a linear arrangement of five platinum atoms bound by pyrophosphite bridges, and two coordinated phosphorous acid molecules on each of the two terminal platinum atoms (Figure 13) (further evidence to support this structure follows):



Note the disparity between the measured and calculated percentages of C and O; again, this was attributed to small contamination of the sample with molecules having different chain lengths (six or seven platinum centers); these complexes would have proportionately higher carbon percentages, as they would require more cations to neutralize charge, and thus lower oxygen

percentages (remember that oxygen was determined by difference).

Spectroscopic Properties

Infrared The infrared spectrum of a KBr mull of the methyltriphenylphosphonium salt of the red polymeric anion is shown in Figure 14. Table 3 details the IR peaks of this anion, along with the assignments for the pyrophosphite dimer and ammonium pyrophosphite; note the proximity of the peaks for all three compounds. This similarity supported the premise that the red compound contained pyrophosphite bridges. The IR stretches for the $P(OH)_3$ groups coordinated to the terminal platinum atoms fell in the same places as those stretches for the pyrophosphite groups, and so no separate peaks were observed.

Table 3. Comparison of Infrared Absorptions of the red complex with $Pt_2(POP)_4^{2-}$ and NH_4POP .			
IR Absorb.	NH_4POP (101)	$Pt_2(POP)_4^{2-}$ (102)	Red
$\nu_{as}(PO)$	1212	1085	1073
$\nu_s(PO)$	1064	910	911
$\nu_{as}(POP)$	908	910*	911*
$\nu_s(POP)$	654	695	665
$\nu(PH)$	---	1320	1307
POH str.	---	---	2355
* obscured by $\nu_s(PO)$ absorption			

UV/Visible The UV/Visible spectrum of the sodi-

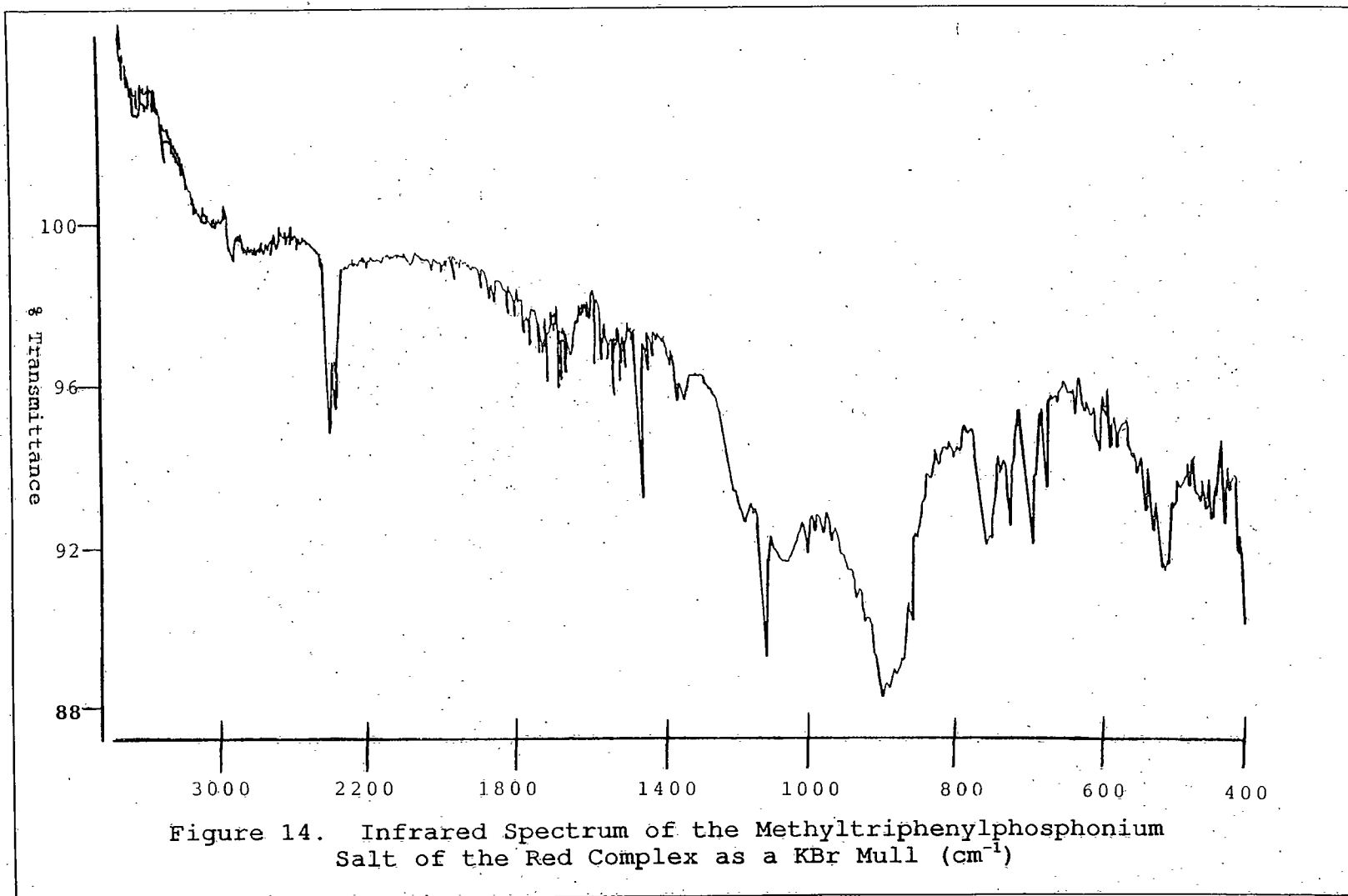


Figure 14. Infrared Spectrum of the Methyltriphenylphosphonium Salt of the Red Complex as a KBr Mull (cm^{-1})

um/potassium salt of the red polymer in water is shown in Figure 15. Figure 16 shows the spectrum of a KBr mull of the sodium salt; note the lack of peaks at 327, 308, 282, and 240 cm^{-1} . These peaks were assigned to hydrolysis products of the red complex formed in water solution. Roundhill reported the UV/Visible spectrum of his darker green compound in 1M HCl, also synthesized at elevated temperature, showed an absorbance at 580 cm^{-1} , compared to 516 cm^{-1} for the red compound (Figure 17.) This difference, in addition to the difference in color, and other properties discussed below, indicated a separate compound than this red anion, despite the apparent similarity in preparation and color.

Fluorescence The results of excitation experiments on KBr mull and aqueous solution are listed in Table 4. Aqueous solutions of the sodium salt were observed to decompose rapidly; over 30 minutes, ten percent of the luminescence intensity was lost.

These data should be compared with the luminescence data obtained for the POP dimer by Gray(103), and Roundhill's trimeric green compound(60). Table 5 details the electronic spectra for these three compounds.

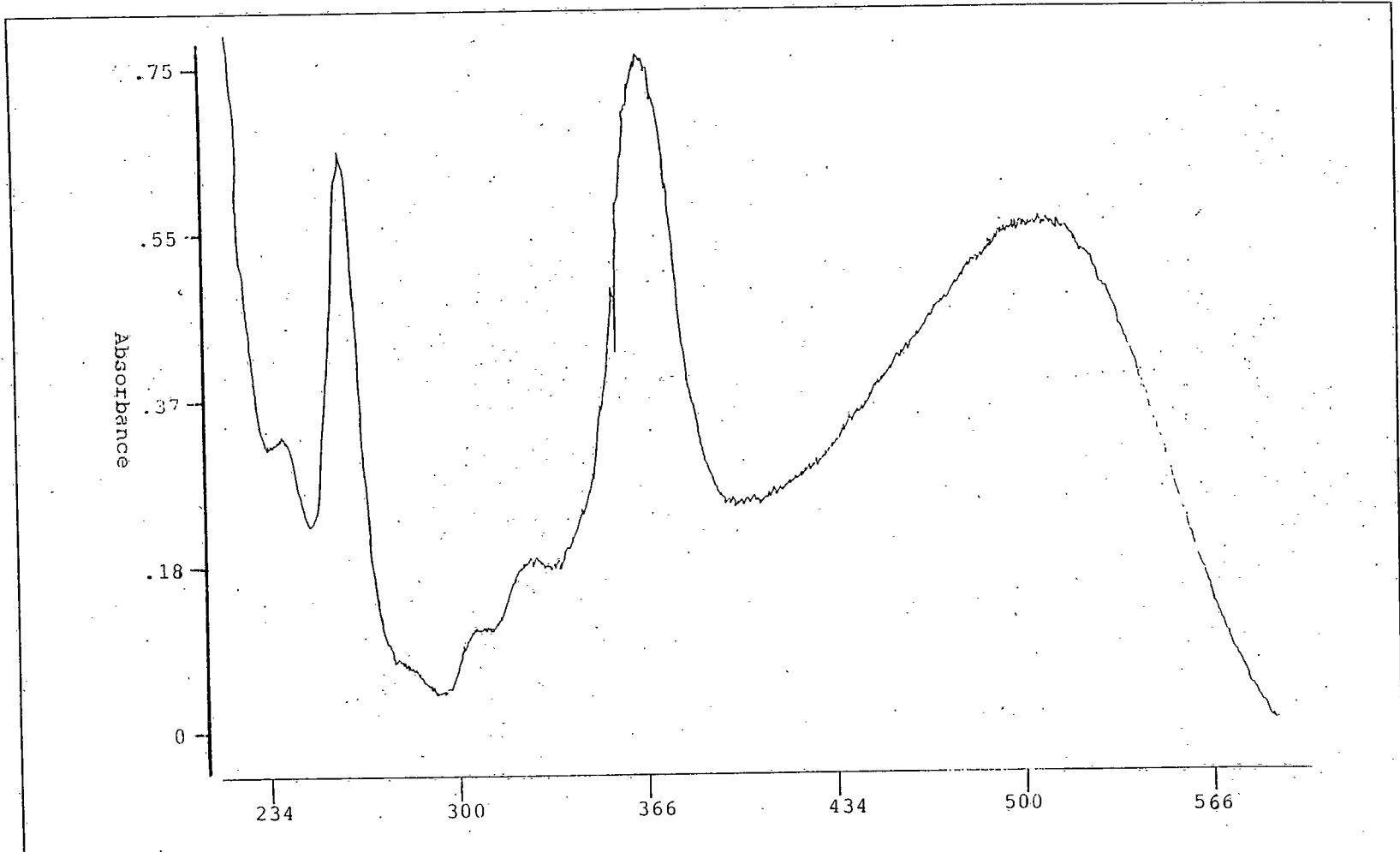


Figure 15. UV/Vis Spectrum of the Sodium Salt of the Red Complex in Water (nm)

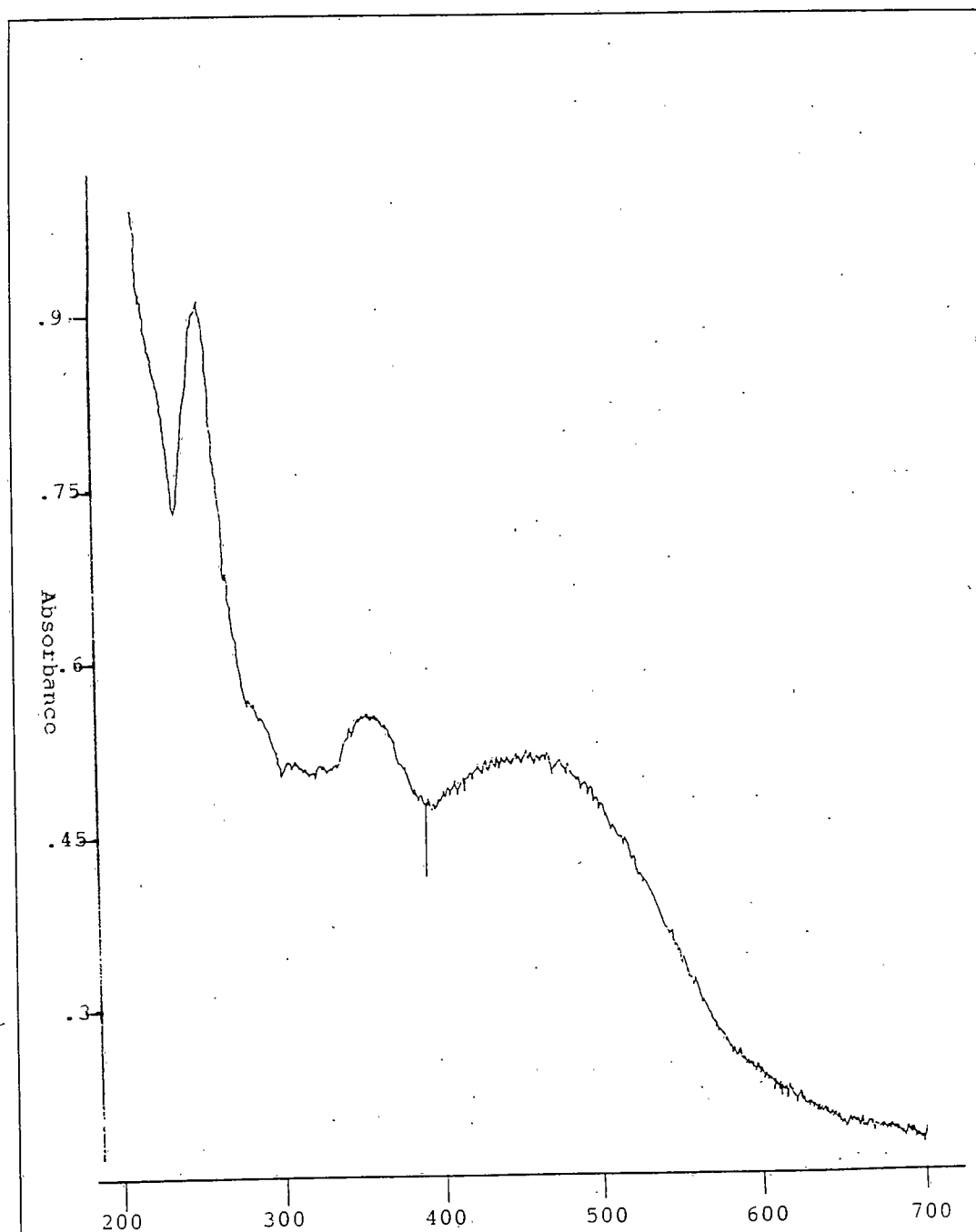


Figure 16. UV\Vis Spectrum of the Sodium Salt of the Red Complex as a KBr Mull (nm)

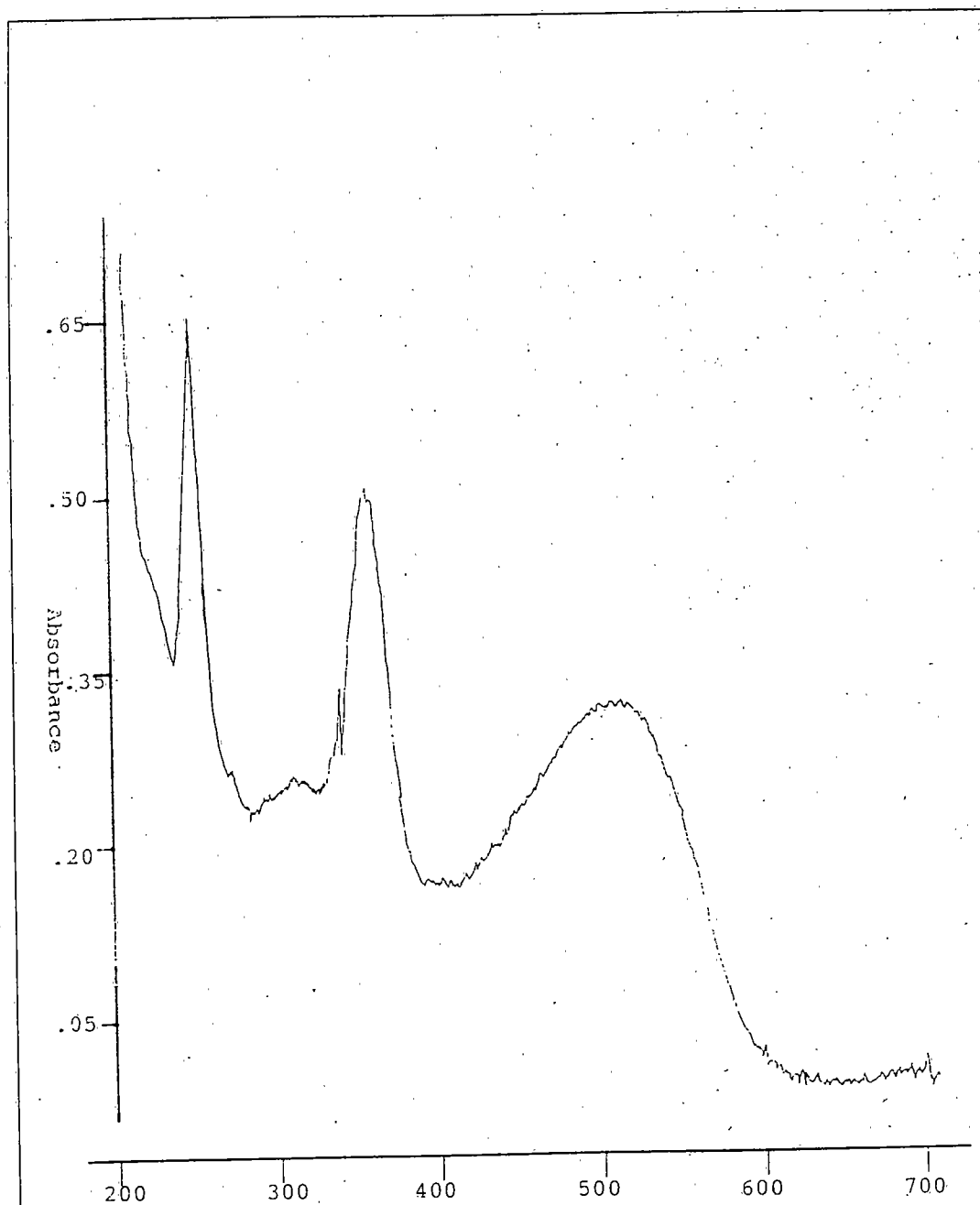


Figure 17. UV\Vis Spectrum of the Sodium Salt of the Red Complex in 1M HCl (nm)

Table 4. Results of Fluorescence Experiments on the Sodium Salt of the Red Complex in a KBr Mull.		
UV/Vis Absorb. Excited		Emissions
Very red appearing sample	265	660
	370	406
		658
		705 (shoulder)
	500	659
700 (shoulder)		
Orange appearing sample	260	630
	365	622
	463	623
Excitation profile	623	430 (shoulder)
		472
		515 (shoulder)

Note that the absorption spectra for the three compounds are very similar (as both solid and in solution), while the direction of emission shift correlates well with chain length of the platinum centers (proposed in the literature (60)) as observed in the rhodium isocyanide complexes in solution.

$Pt_2(POP)_4^{4-}$		$Pt_3(POPOP)_4^{6-}$		red complex	
Absorb.	Emmis.	Absorb.	Emmis.	Absorb.	Emmis.
285 (270)	----	≈270	----	265	660
345 (303)	----	----	----	----	----
368	403 514	368	650	370	406 658
452	----	580	650	500	659

NMR Spectroscopy The hydrolysis of the red complex in aqueous solution proved impossible to overcome in obtaining NMR spectra in water; only the resonances due to the monomeric POP substituted complex and the POP dimer were observed. However, the solubility of some salts of the complex in organic solvents did allow spectra to be collected. Figure 18. shows the ^{31}P NMR spectrum of the methyltriphenylphosphonium salt in DMSO; note the broadness of the complex resonance centered at 62.1 ppm, due to small differences in the environments of a great many similar phosphorus atoms; the proposed structure has phosphorus atoms in four different environments, each coupled to at least one, and for some of the phosphorus atoms, two platinum atoms. The equally broad satellites ($^1J P-Pt = 3300$ Hz, essentially the same as the coupling constants reported for the POP dimer and the

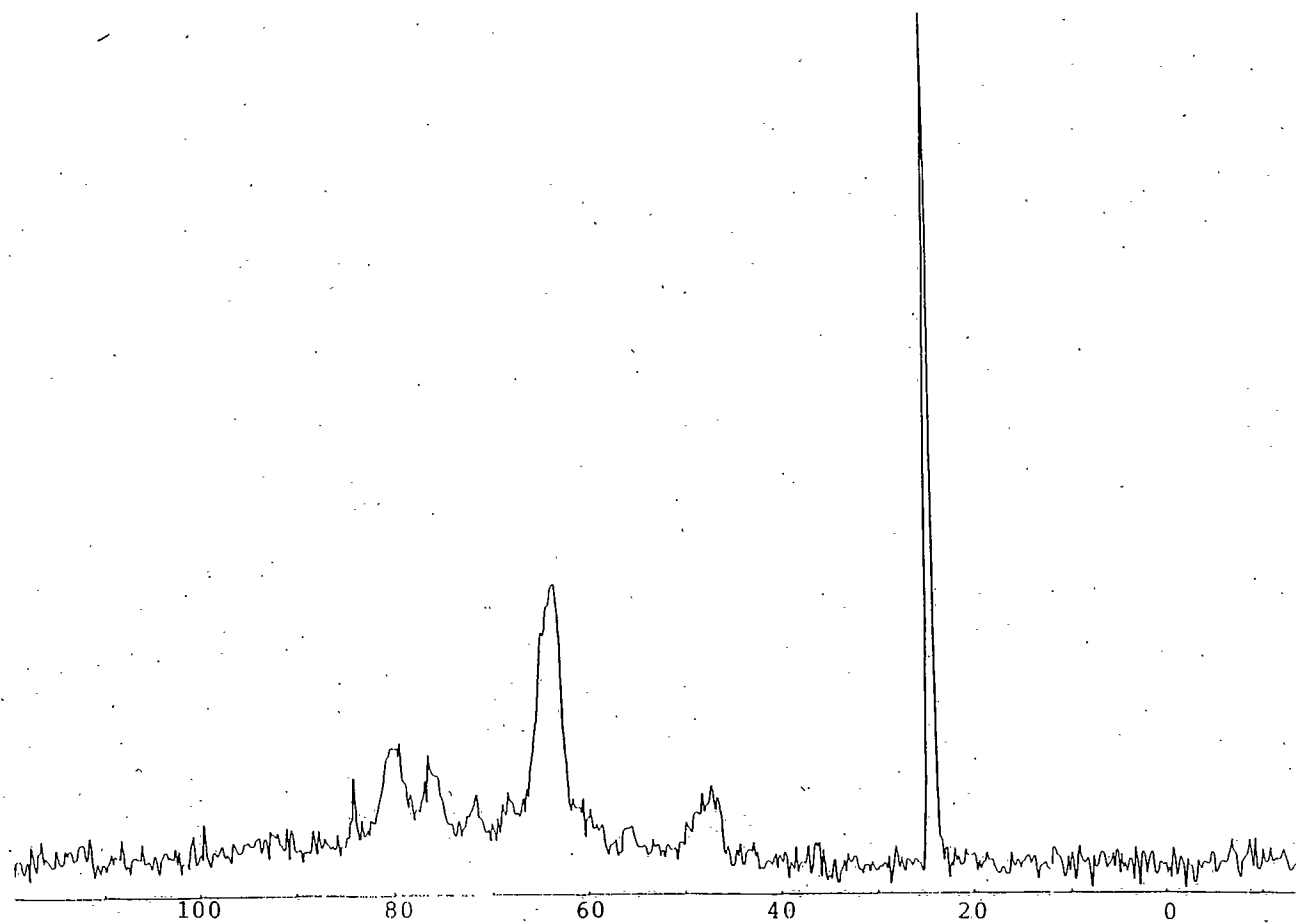


Figure 18. ^{31}P NMR Spectrum of the Methyltriphenylphosphonium Salt of the Red Complex in DMSO; line broadening= 50 Hz.

'POPOP' dimer of 3250 and 3300 Hz, respectively) indicate that the phosphorus atoms are all bound to platinum atoms, supporting an extended chain interaction between the phosphorus and platinum atoms. Also note the presence of the resonances due to the monomeric and dimeric POP species; the terminally bound $P(OH)_3$ groups would be expected to have nearly identical chemical shifts as the monomer complex, and so the broad resonance at 75.3ppm, with satellites at 70.4 and obscured under the satellite for the red complex at 78.7 ($^1J_{P-P} = 992\text{ppm}$) was assigned to those phosphorus atoms, while the presence of the dimer peak indicated that even in distilled, dried DMSO enough water is present to hydrolyze some of the red complex to the dimer.

The resonance at 62.1 ppm in the ^{31}P NMR spectrum is the same as that reported by Roundhill for his green 'POPOP' trimer(60). Roundhill reported the vermilion red compound to be insoluble in organic and aqueous media, while our red complex was quite soluble in aqueous media; while it may be possible for the same system to provide two different species exhibiting red color and luminescence, Roundhill's vermilion red compound is probably the same compound as here described. The green 'POPOP trimer', however, while its reported solubility and electronic properties show it to be similar to our red complex, must be different from it.

Figure 19 shows the ^{31}P NMR spectrum of the sodium salt dissolved in methanol; the monomer and dimer are still present, as well as a myriad of new resonances with platinum satellites. These species are approximately centered about 83 ppm, with $^1\text{J P-Pt}$ ranging from 3194 to 3282 Hz.

The chemical shift of the broad resonance in DMSO is slightly downfield from the resonance of the POP dimer in water, while the chemical shift of the multiple peaks is somewhat upfield from the resonance of the monomeric POP complex. These chemical shifts indicated that the multiple peaks were due to phosphorus atoms bound in monomeric platinum complexes, while the broad resonance must have been due to phosphorus atoms in a molecule very much like the POP dimer. Thus the multiple resonances must be due to monomeric decomposition products of the red species having interacted with methanol (the same results were observed for 10% acetonitrile/methanol) or the water in these solvents, while the broad resonance was due to a large, extended chain molecule with bridging phosphorus atoms present in a form like pyrophosphate, as the proposed structure contains.

The multiplicity of the monomeric peaks told us the sort of molecule the red compound must be to decompose to provide so many species. The red anion, formed by dehydration of phosphorous acid, seemed to be a large

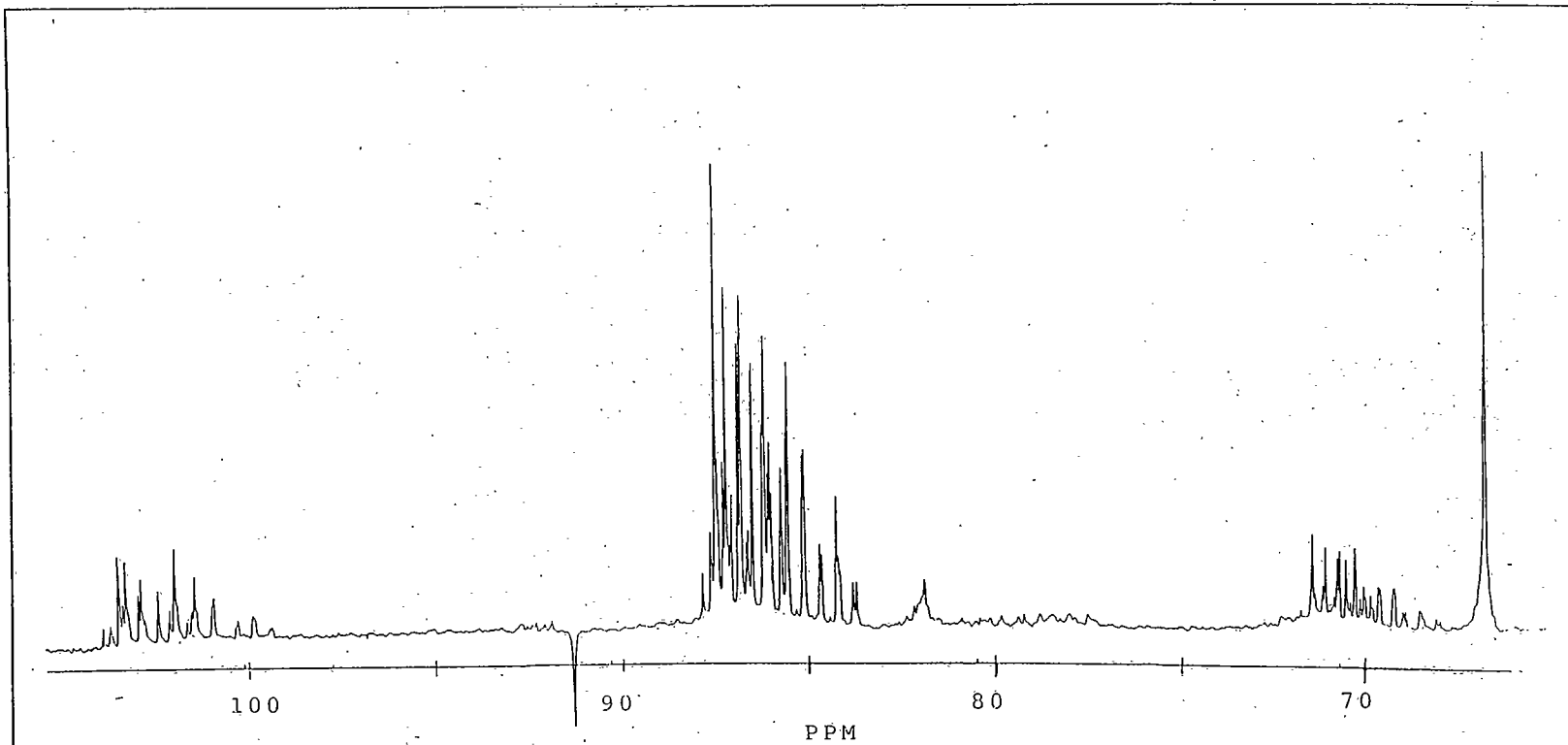


Figure 19. ^{31}P NMR Spectrum of Decomposition Products of the Sodium Salt of the Red Complex in 10% $\text{CH}_3\text{CN}/\text{CH}_3\text{OH}$.

oligomer of platinum atoms bound by POP-type bridges; these bridges could consist of longer dehydrated molecules, such as triphosphite (POPOP), due to the high temperature at which the complex was formed, but the elemental analysis results, and lack of POPOP resonances in the ^{31}P NMR spectra, excluded this possibility. As this polymer of platinum bound phosphorus atoms began to decompose due to re-hydration of the phosphorus bridges (apparently slow enough in methanol to allow observation of the many resonances), clearly a very complicated mixture of platinum complexes would result; these compounds would consist of partially hydrated complexes containing four, three, or two platinum atoms, with a variety of arrangements of bound phosphite/pyrophosphite ligands, as well as the monomeric complex we already observed. The interactions between the platinum atom(s) and all these different phosphorus atoms would lead to a very complicated mixture of species with very similar phosphorus resonances, as we here observed.

No ^{195}Pt NMR resonances were ever observed (further indication that we are not observing the same compound Roundhill reports). This must be due to the complexity of the multiple platinum resonances coupled to each other for the three different kinds of platinum atoms in the molecule, as well as the added coupling to the different phosphorus atoms, having the effect of broadening the

resonances into the baseline. The phosphorus resonances were observed because of the higher natural abundance of the element, and the presence of four times as many phosphorus atoms as platinum atoms.

XPS The X-ray photoelectron spectrum of the potassium salt of the red complex showed the binding energy for the $4f_{7/2}$ platinum electron to be 72.6 eV (Figure 20.), and that for the phosphorus P-2p electron to be 132.6 eV (Figure 21.) These binding energies were obtained from the spectra by subtracting the plotted peak energy in electron volts from the energy of the radiation used for analysis-- 1253.6 eV. The platinum energy was about 1.1 eV lower than the energy reported for the POP dimer, but was still well within the range for platinum bound to phosphine and phosphite ligands.

The phosphorus binding energy for the POP dimer and the platinum(II) axially substituted dimers are reported to range from 133.4 to 133.9 eV, while the value for the phosphorus in the red compound was about 1 eV lower, at 132.6 eV. This could indicate a slight change in the ligand, such as a mixture of POP and $P(OH)_3$, might provide, but is still well within the range for these types of phosphorus compounds.

Solution Stability

Potassium salt The red, red luminescent solid was

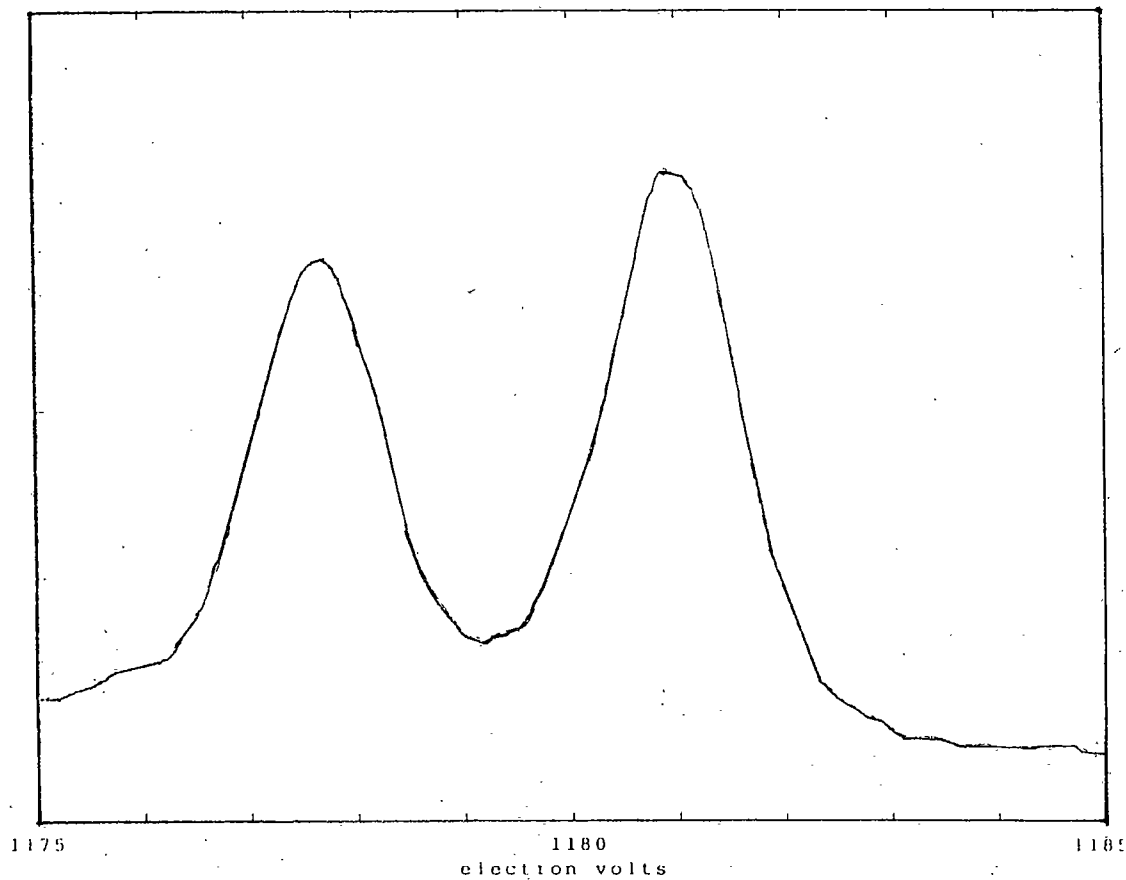


Figure 20. Platinum X-ray Photoelectron Spectroscopy Spectrum of the Methyltriphenylphosphonium Salt of the Red Complex

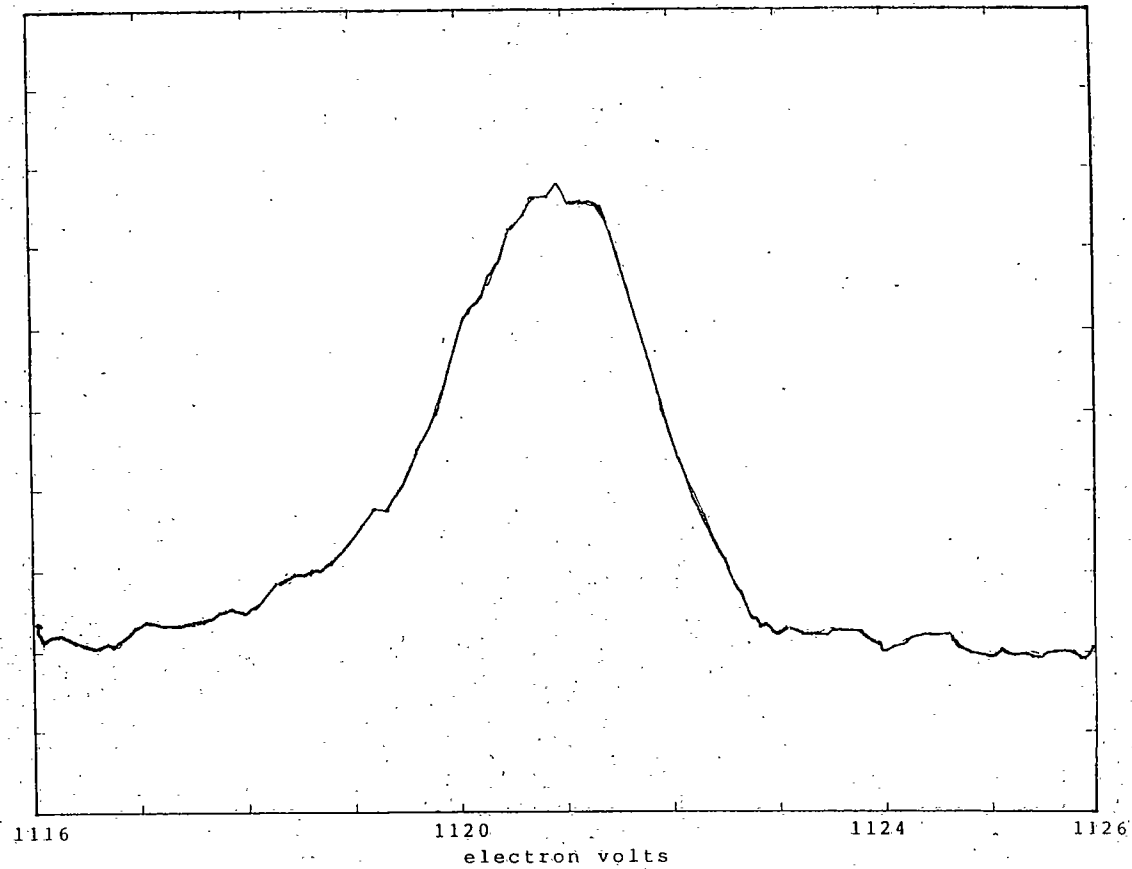


Figure 21. Phosphorus X-ray Photoelectron Spectroscopy Spectrum of the Methyltriphenylphosphonium Salt of the Red Complex.

very soluble in water, and decomposed quickly (see above); it was also soluble in diethylphosphite, ethylene glycol, DMSO and DMF, producing red to orange/green solutions (for ethylene glycol), which luminesced orange to green. DMSO and DMF solutions could be very stable, remaining dark red with red/orange luminescence for several months.

The solubility of the red complex in non-aqueous media appeared to be very dependent upon the presence of residual acid as phosphorous acid. Some preparations appeared to be totally insoluble in the above solvents until small amounts of phosphorous acid were added. In addition the presence of the acid seemed to stabilize the complex, in that preparations with low solubility also showed much less red and more green color and luminescence.

Sodium Salt The sodium salt behaved much like the potassium salt in its solubility characteristics, with the exception of solubility in more organic solvents; this salt was somewhat soluble in wet methanol and acetone, and 10% acetonitrile/methanol, as well as DMF and diethylphosphite, giving red/orange solutions with orange luminescence. If the solid was dried in a drying pistol overnight, it was insoluble in all the organic solvents but DMF. The solubility in non-aqueous solvents was even more dependent upon acid presence than for the

potassium salt; 30 mg of solid in 2 mL of DMSO and DMF each produced pale red solutions; addition of one drop of water made the solutions paler, but a few drops of a saturated aqueous solution of phosphorous acid caused the solution to turn much redder, with orange luminescence. One preparation dissolved in bulk acetone gave a moderately dark red solution upon addition of phosphorous acid; the solution turned yellow/orange, with pale green luminescence upon addition of one drop of water.

An old sample of the salt (which had turned orange) was insoluble in 10% acetonitrile/methanol until a little phosphorous acid was added, at which point the solid became red and red luminescent, with a green luminescent solution; this solid was insoluble in all organic solvents except DMSO and DMF, which produced pale green solutions.

Methyltriphenylphosphonium Salt The solution behavior of the nitrate and bromide methyltriphenylphosphonium salts were identical: insoluble in water and most organic solvents; only DMF, DMSO and sulfolane provided relatively concentrated red, red luminescent solutions. Weak solutions were observed in diethylphosphite (pale red solution and luminescence, but after 15 minutes the luminescence disappears, and purple solid precipitates), methanol, 10% acetonitrile/methanol, and acetonitrile (orange to red solution, orange lumines-

cence), acetic acid (pale orange solution and luminescence, but turn green), and formamide (green solution and luminescence.)

X-ray Crystallography

In no case were any crystals of the red anion obtained of suitable quality for X-ray analysis. The only such crystals collected were derivatives of the red complex formed by reaction with the halide counter-ions of large cations (like $(\text{Bu})_4\text{NCl}$ or $(\text{CH}_3)_4\text{NBr}$) added to try to form crystals of the red anion.

Aqueous solutions of the potassium salt of the complex formed green metallic needles with $(\text{CH}_3)_4\text{NI}$, and orange to red needles with $(\text{CH}_3)_4\text{NBr}$ and $(\text{Bu})_4\text{NBr}$. Solution of the structures of these derivatives gave the dihaloaxially substituted POP dimers, $\text{Pt}_2(\text{POP})_4\text{I}_2^{2-}$ (unit cell 16.0086, 16.8876, 16.3354) and $\text{Pt}_2(\text{POP})_4\text{Br}_2^{2-}$ (unit cell 15.2880, 15.2921, 11.6217), with no differences in the anion structure from that reported. Crystals were obtained appearing to be of the red compound (red color, red phosphorescence), but were found to be phosphorous acid contaminated with small amounts of the red complex.

Crystallization Attempts

Aqueous Solvents Many separate attempts were made at crystallizing the red luminescent cation from aqueous solution using large anions or liquid/vapor diffusion of

organic solvents. In every case but the two mentioned above, no crystals of sufficient quality for study by x-ray diffraction were obtained; see Table 6 for details and results.

Method	Results
Ba(NO ₃) ₂	cloudy, orange luminescence
Rb(CO ₃)	yellow, no luminescence
Rb(CH ₃ COO) ₂	orange, no luminescence
Sr(NO ₃) ₂ , SrCO ₃ , Sr(CH ₃ COO) ₂	orange, no luminescence
Al(CH ₃ COO) ₃	burgundy, no lumin.
(NH ₃) ₂ CO ₃	yellow, no luminescence
Li ₂ CO ₃	orange, no luminescence
(Bu) ₄ NNO ₃ , also low temp.	orange, orange lumin.
(Bu) ₄ NCl, also low temp.	orange and red crystals
(Bu) ₄ NClO ₄ , also low temperature	lavender solid
(Bu) ₄ NI, also low temperature	yellow spindles, and green metallic spindles
(Bu) ₄ NBr, also low temp.	orange and red crystals
(Me) ₄ NBr, also low temperature	yellow and red spindles, and red crystals
(Me) ₄ NI, also low temperature	green and yellow spindles
(Me) ₄ NNO ₃ , also low temp.	red luminescent solid
(Me) ₃ N·HCl	ruby red solution
NH ₂ CH ₂ CH ₂ NH ₂ ·HCl	red, red luminescent solid

Table 6., continued.	
Method	Results
(Eth) ₂ N·HNO ₃ , also low temperature	orange, orange luminescent solution
(Eth) ₂ N·2HCl, also low temperature	red, and green metallic solid
(Ph ₄ As) ₂ CH ₂	yellow solution, green luminescence
(Ph) ₄ AsNO ₃	burgundy solution
Me(Ph) ₃ PBr, Me(Ph) ₃ PNO ₃ ; diffusion, layering (acetone or methanol solution)	red, red luminescent solid; yellow spindles
degassed water	no solid

Non-aqueous Solvents Because of the hydrolysis of the red compound in water, non-aqueous solvents seemed a promising way in which to obtain crystals; Tables 7, 8, and 9 list the results of attempts. In all cases, no solid of sufficient quality for crystallographic analysis was obtained. In a single case, a solution of the sodium salt of the red compound in acetone precipitated red luminescent crystals, which proved to be a form of phosphorous acid contaminated with the red compound.

Table 7. Results of Attempts to Grow Crystals of the Sodium Salt of the Red Complex in Non-aqueous Media for X-ray Diffraction Analysis (conducted at room temperature unless noted.)

Solvent	Results
Methanol with H_3PO_3 , low temperature	red, red luminescent crystal
acetone, low temperature	no solid
acetone, evaporation	green solid
DMSO, Me_4NNO_3	red solution, no solid
DMSO, $Ph_4AsCl \cdot HCl$	red solution, no solid
DMSO, saturated $H_3PO_3(aq)$	redder solution, no solid
DMSO, layer with cyclohexylamine	yellow solution, no solid
DMF, saturated $H_3PO_3(aq)$	redder solution, no solid
DMF, $Ph_4AsCl \cdot HCl$, low temperature	red luminescent solid
DMF, Me_4NNO_3	flocculent orange solid
DMF, $MePh_3PNO_3$, layer with benzene	red solid

Table 8. Results of Attempts to Grow Crystals of the Potassium Salt of the Red Complex in Non-aqueous Media (room temperature unless otherwise noted).

Solvent	Method	Results
DMSO	$MePh_3PNO_3$, layered with ether, acetone	peach solution, orange luminescence
$(Et)_2POH$	layer with ether	no solid
	layer with benzene	no solid
	layer with ethylene glycol	no solid
	layer with toluene	no solid

Table 8., continued.		
Solvent	Method	Results
(Et) ₂ POH	layer with CCl ₄	no solid
ethylene glycol	layer with ether	red solution, green luminescence, no solid

Table 9. Results of Attempts to Grow Crystals of the Methyltriphenylphosphonium Salt of the Red Complex for X-ray Diffraction in Non-aqueous Media.		
Solvent	Method	Results
CH ₃ OH	cool hot saturated solution	yellow to red solution
	layer with ether	yellow solution
	vapor diffusion of ether at low temperature	red solid (5 days)
10%CH ₃ CN/CH ₃ OH	layer with ether, isopropanol, cyclobenzene; mix acetone	yellow solution, orange luminescence
CH ₃ CH(CH ₃)CH ₃	cool hot saturated solution	none
DMSO	few drops conc. HNO ₃ , HOAc, H ₂ SO ₄	colorless, hot
	layer at low temp. with acetone, ether, benzene, toluene, CH ₂ Cl ₂	red to orange solutions, no solids
	KSCN	pink, green lumin. solution
	NaCN	yellow solution
	Ph ₄ AsNO ₃ Me ₄ NNO ₃ Bu ₄ NNO ₃	yellow to orange solutions, no solids

Table 9., continued.		
Solvent	Method	Results
DMSO	Ph ₃ P	colorless solution, no solid
	Et ₂ NCSNa	yellow solution
	Ethylenediamine	dark solution
	pump off solvent	no volume loss in two weeks
DMF	pump off solvent	green, red solid
	cool saturated solution	red solution, no solid
	layer with 95% ethanol, absolute ethanol, ether	orange solution, no solid
Formamide	cool saturated solution	green, green lumin. solution
Sulfolane	cool saturated solution	red, green lumin. solution
H ₃ PO ₃	melt	yellow, green lumin. solution

Reactions

The methyltriphenylphosphonium salt of the red anion was dissolved in DMSO and reacted with several different ligands and acids (Table 10.) These reactions probably reflect decomposition of the oligomeric red complex to form axially substituted POP dimeric molecules, and variously substituted monomeric complexes.

Table 10. Results of Reactions of the Methyltriphenylphosphonium Salt of the Red Complex.

Solvent	Method	Results
DMSO	excess KSCN, heat KSCN, room temp.	yellow, green luminescence
	conc. CH ₃ COOH, heat	brown, green luminescence
	conc. HNO ₃ , H ₂ SO ₄	colorless, hot
	P(C ₆ H ₅) ₃	no reaction
	NaCN	yellow solution
	NH ₂ CH ₂ CH ₂ NH ₂	dark yellow, green lumin.
	(CH ₃ CH ₂) ₂ NCS ₂ Na	yellow, green luminescence
	(CH ₃ CH ₂ O) ₂ POH	orange solution and luminescence
pH 7 PO ₄ ³⁻ buffer	NaCN	yellow solution
(CH ₃) ₂ CH ₂ OH	(CH ₃ CH ₂) ₂ NCS ₂ Na + heat	yellow, green luminescence
melted H ₃ PO ₃	-----	yellow, green luminescence

A polymeric, pyrophosphite bridged platinum(II) complex has been characterized by elemental analysis, spectroscopic properties, and reaction chemistry, and a structure proposed. We will now consider the formation of the sulfato- and phosphato- Pt₂X₄²⁻ dimeric complexes by a reaction scheme the reverse of disproportionation.

The Concept of Reverse Disproportionation

Much of the synthesis of coordination compounds involving intermolecular metal-metal interactions has

been fortuitous (Chapter I); in an accidental fashion a soup of proper reagents has allowed the isolation and characterization of novel multinuclear clusters. While providence is always appreciated, it is desirable to make new compounds with multiple metal atom cores in a more reasoned, systematic approach; if the scales can be weighted by design to direct a series of reactions toward a goal compound, we can introduce small changes in a process, examine the resulting products, and then alter again the procedure until we understand how a given group of compounds form.

Many of the platinum metal clusters discussed in the introduction were discovered accidentally; of particular interest in the work that follows are the phosphate/sulfate platinum(III) dimers, $\text{Pt}_2(\text{SO}_4)_4^{2-}$ and $\text{Pt}_2(\text{HPO}_4)_4^{2-}$, made from the reaction of platinum(II) with the strongly oxidizing mineral acids H_2SO_4 and H_3PO_4 . After proceeding through several color changes, products are isolated; these colors indicate that several probably complex intermediate steps precede formation of the dimeric products. These steps surely play an important role in the observed variability of product yield, and the difficulty in reproducing results. If we imagine a simple scheme by which we could make these compounds directly, the reproducibility of the synthesis and yield should be improved.

The sulfate and phosphate platinum(III) dimers are formed with the reaction of the tetranitritoplatinate(II) ion with oxidizing acids(36); brown gas is evolved at stages throughout the color changes of the reaction. The formation of NO_2 gas, as well as a platinum(III) product from platinum(II) starting material, prove that some redox processes are going on. Crystals isolated by Peterson and Min from the soup of intermediates support this conclusion as well(47,48), for the compounds have coordinated nitrosyl groups, the result of partially reduced nitrite ion. It seems reasonable to conclude that as the nitrite ion is reduced to nitric oxide gas, and then dissociates from coordination with the metal, that a platinum(II) is oxidized to platinum(IV). It is plausible, then, that a platinum(IV) ion and a platinum(II) ion may combine to form two platinum(III) ions, in a scheme like the reverse of disproportionation(48). Perhaps the dimers can be made by a more direct method, such as this. If this scheme occurs, then the appropriate platinum(II) and platinum(IV) starting materials, reacted with sulfate and phosphate, should provide the desired platinum(III) dimeric products.

These thoughts suggest a series of direct experiments to see if this reaction scheme might indeed work; it is sensible to do experiments on the known compounds to see what they can tell us. If we can learn

more about the mechanism of dimer disproportionation, this might shed some light as to how they may be formed by the reverse of disproportionation.

Reactions with Hydrochloric Acid

When the platinum(III) dimers decompose, what products are obtained? Two possibilities exist-- either new platinum(III) compounds form, or separate platinum(II) and platinum(IV) compounds form. Since chloride ion is a good ligand for platinum, and the platinum NMR spectra of PtCl_4^{2-} and PtCl_6^{2-} are well understood (104), (105), (106) reaction of the dimer unit with concentrated hydrochloric acid is an obvious choice.

A solution of $\text{K}_2\text{Pt}_2(\text{SO}_4)_4$ was made by dissolving 25.8 mg of the dimer in 2 mL of D_2O , and the platinum NMR spectrum obtained (Figure 22); no other peaks were observed. Approximately one-half mL of concentrated hydrochloric acid was added, and the solution heated (color changed to yellow/orange from pale orange.) Figure 23 shows the resulting NMR spectra of the three regions (platinum(III), platinum(IV), and platinum(II).) Identical results were obtained for the phosphate dimer; the dimer disproportionated in hydrochloric acid to form equimolar quantities of platinum(II) and platinum(IV), without the formation of detectable intermediate species.

So, the platinum(III) dimers undergo facile disproportionation to form platinum(II) and platinum(IV) species.

Reactions with Barium Ion

How stable are the platinum(III) dimers? HCl is quite a vigorous environment in which to decompose these complexes; what if less strenuous conditions are used? For instance, how many bridges are required to hold the dimeric unit together? If the complexes are durable enough to hold together with only one or two bridging ligands, we could use such molecules as building blocks to construct new complexes.

A solution of the sulfate dimer in water was treated sequentially with equimolar amounts of barium perchlorate, reasoning that a shift in the platinum NMR resonance of the dimer peak would be observed as one, then two, and perhaps three sulfate bridges were removed from the complex, until the complex fell apart to yield a platinum(II) resonance and a platinum(IV) resonance.

The results of these experiments in water, and in 1M HClO₄ (to stabilize platinum(II) complexes(106)), were identical. Even with the addition of one equivalent of barium ions, the resonance of the dimer peak slowly decreased over 36 hours until the resonance was gone (Figure 24.) Additionally, no new resonances arose in

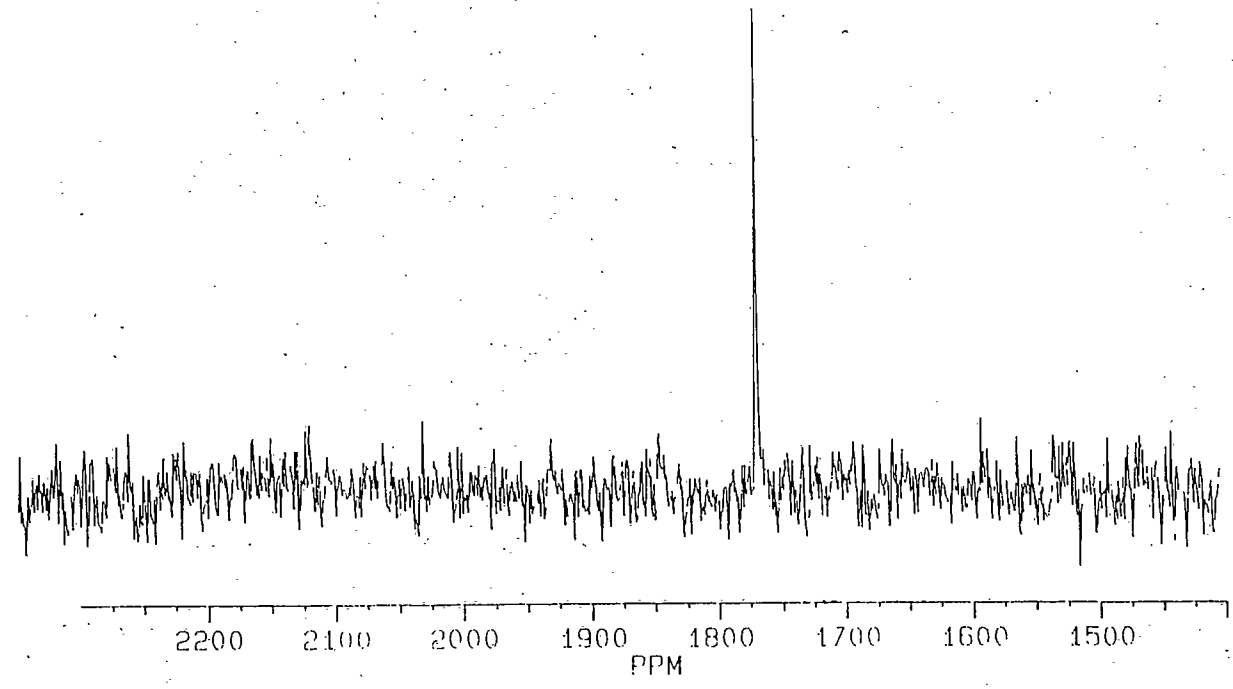
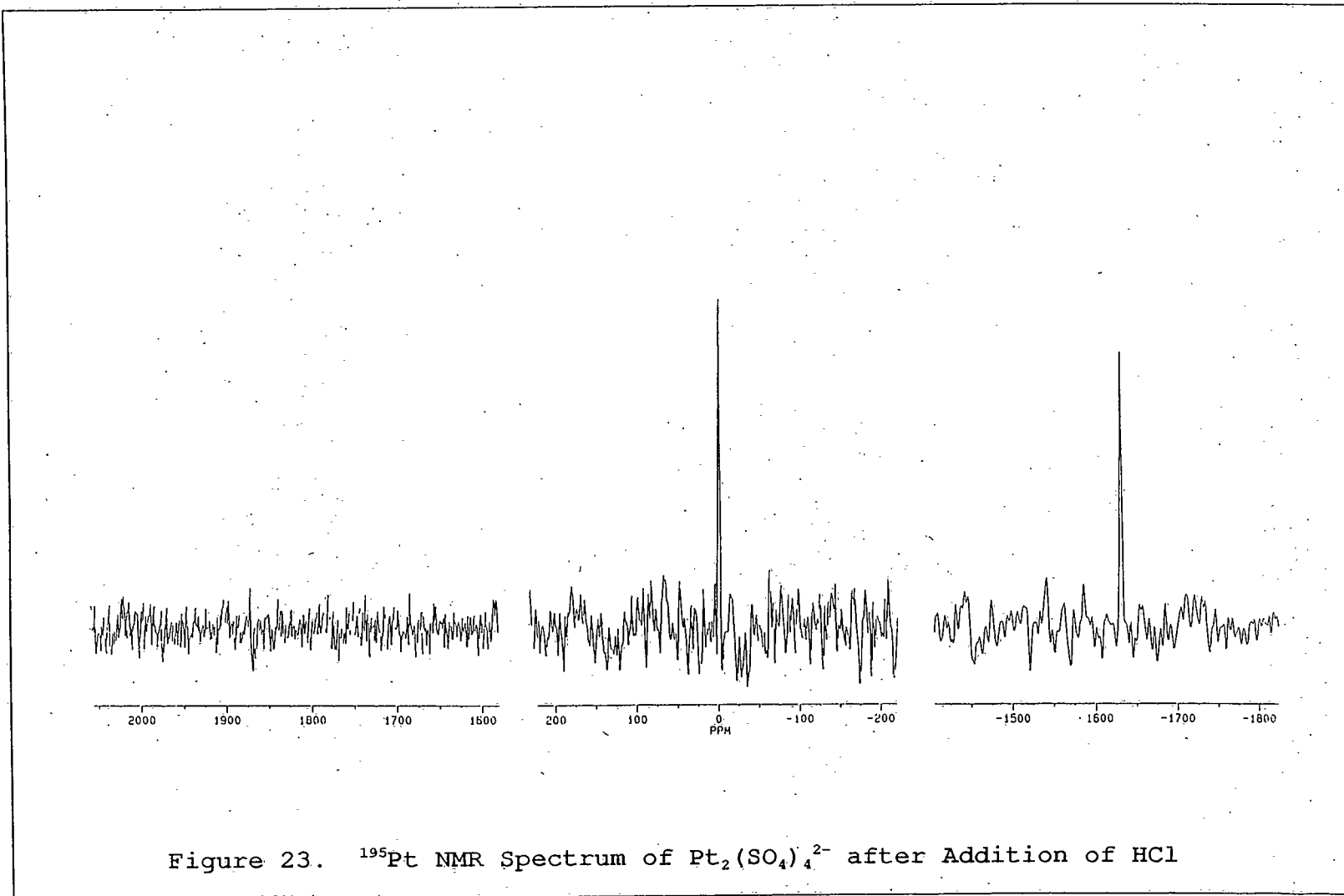


Figure 22. ^{195}Pt NMR Spectrum of $\text{Pt}_2(\text{SO}_4)_4^{2-}$ in Water



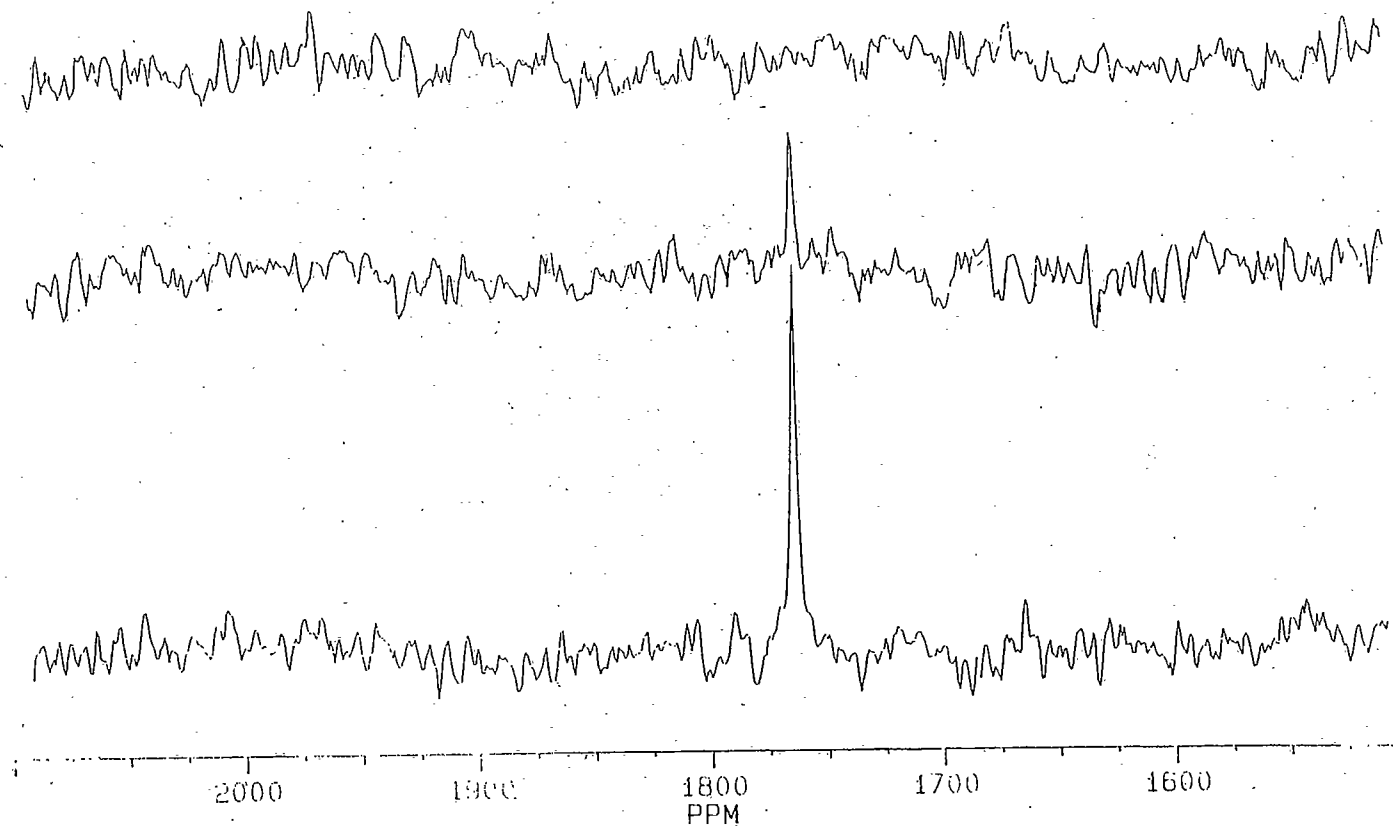


Figure 24. Loss of the ^{195}Pt NMR Resonance of $\text{Pt}_2(\text{SO}_4)_4^{2-}$ upon Addition of One Equivalent of Ba^{2+} Ion. Bottom 1 Hr. Old, 18Hrs., Top 36 Hrs.

either the platinum(II) or platinum(IV) regions, suggesting that the decomposition products of the dimer are not simple, mononuclear complexes (for we would have seen their resonances) unless a very strongly interacting ligand is present (like chloride). Perhaps the lack of resonances is due to the formation of a polymeric species as discussed in Chapter I, whose platinum NMR resonance is broadened so much it is unobservable.

These experiments suggest that it will not be possible to form partially bridged (less than four bridges) complexes to lead to new complexes with a mixture of different bridges, such as $\text{Pt}_2(\text{SO}_4)_2(\text{HPO}_4)_2$ or the like.

Reactions with Aqueous Sulfate Ion

The platinum resonances of solutions of the $\text{Pt}_2(\text{X})_4^{2-}$ dimers in water or D_2O were found to decrease in intensity over one to two months; no new peaks appeared. It was thought this might be due to slow dissociation and loss of the bridging ligand, resulting in complex decomposition (as demonstrated above.) Perhaps if the ligand concentration in solution were high, enough bridging molecules would be available to replace a dissociated ligand and the dimer would be stabilized.

To test this idea, solutions of 2 M Li_2SO_4 in water were prepared, into which the dimeric sulfate was

dissolved (frequently requiring heating); the same results observed for aqueous solution were observed for these sulfate solutions-- loss of the dimer resonance over one to two months, with the appearance of no new resonances. Solutions of the platinum(III) sulfate dimer in perchloric acid with 2 M Li_2SO_4 behaved similarly. Evidently polymerization of the complexes is not affected by anything but the most stabilizing ligands (like chloride.) Even solutions of the dimer in its concentrated acid, containing 16-18M ligand, lose resonances over the same time span.

This appears to be a contradiction! How can the platinum(III) dimers form in an environment in which they seem to be unstable; i.e., $\text{Pt}_2(\text{SO}_4)_4^{2-}$ forms in concentrated H_2SO_4 , yet decomposes over one to two months in the same environment. It seems that the dimers must be merely long lived, relatively stable intermediates on a path to larger order oligomers. This is consistent with the low and variable yields of the literature preparations of these compounds-- under slightly different conditions one would expect the equilibrium required to precipitate the platinum dimers would be disrupted; under proper conditions the intermediates of the reaction precipitate from solution and can be isolated, but when the conditions are not met the reaction proceeds to the large polymeric products. It

appears that $\text{Pt}_2(\text{SO}_4)_4^{2-}$ and $\text{Pt}_2(\text{HPO}_4)_4^{2-}$ could be only the first step intermediates on the path to large polymeric complexes (85, 92-95).

We now know that the dimeric units do not hold together with less than four bridges; in the absence of a strongly coordinating ligand like chloride the products of dimer decomposition appear to polymerize to form molecules with unobservable platinum resonances, and with a strongly coordinating ligand like chloride the result of decomposition is disproportionation of the platinum(III) dimer to form PtCl_4^{2-} and PtCl_6^{2-} .

From these results it appears that reverse disproportionation might well be a way in which to tackle the systematic formation of dimeric compounds similar to $\text{Pt}_2(\text{SO}_4)_4^{2-}$ and $\text{Pt}_2(\text{HPO}_4)_4^{2-}$, if we can find the appropriate platinum(II) and platinum(IV) starting materials that avoid these polymerization problems and lead directly to the dimers. What characteristics should these starting materials have? They should exist as stable, simple mononuclear species in acidic solutions (because the literature preparations occur in strongly acidic media), and preferably basic solutions as well (to give some flexibility in reaction conditions), so reactants can be easily characterized and tracked by platinum NMR spectroscopy; they should also contain weakly coordinating ligands (such as NO_3^- , CF_3SO_3^- , $\text{OH}^-/\text{H}_2\text{O}$, or the like),

so that when the desired ligands (sulfate and phosphate) are added, the starting ligands will be easily replaced.

The first step is to determine what compounds would be appropriate for the platinum(IV) and platinum(II) reactants by studying the stability of variously substituted complexes in acid and base.

The Nature of Platinum(IV) in Acid Solution

We need to find a platinum(IV) species which is stable in strong acid, and has a ^{195}Pt NMR spectrum so we can observe changes in the species as it reacts (we expect) with a platinum(II) complex to form a platinum(III) dimer. As a first try, $\text{K}_2\text{Pt}(\text{OH})_6$ seems reasonable, for the crystal structure and ^{195}Pt NMR resonances have been reported (104), (107), (108). The compound is formed in very basic solution; dissolution in strong acid might be expected to protonate some of the coordinated hydroxide, but otherwise yield a well behaved compound which might substitute coordinated water/hydroxide with sulfate or phosphate, and so provide a precursor to the platinum(III) dimers.

In the following experiments, platonic acid was used interchangeably with $\text{K}_2\text{Pt}(\text{OH})_6$; by platonic acid we mean the yellow, neutral solid which is precipitated from basic solution, but is not recrystallized to yield

$K_2Pt(OH)_6$. The amount of protonation of this compound is unknown, as is the structure; it could be a simple monomeric molecule like $K_2Pt(OH)_6$, or it might be some kind of network(93-96). In either case, the reaction behavior of both the recrystallized $Pt(OH)_6^{2-}$ and platinic acid were found to be the same.

Formation of Solids with Strong Mineral Acids

Solutions of $K_2Pt(OH)_6$ or neutral platinic acid in strong mineral acids (phosphoric, sulfuric, perchloric, nitric, or trifluoromethanesulfonic acid) all formed red/orange precipitates. This agreed with earlier reports (93), (94). The rate at which these solids formed depended upon the acid used; for sulfuric and perchloric acids, the precipitates formed very rapidly (one to two minutes at room temperature for the concentrated acid), while the remaining acids reacted more slowly (as long as overnight for concentrated phosphoric acid). Reactions with concentrated acetic acid behaved differently, causing the solutions to turn black as the mixture was heated; no reaction occurred at room temperature.

Variation of platinum concentration seemed to have no effect on the formation of the precipitates; acid concentration, however, did have a small influence. At room temperature, low acid concentration of 0.01M or less

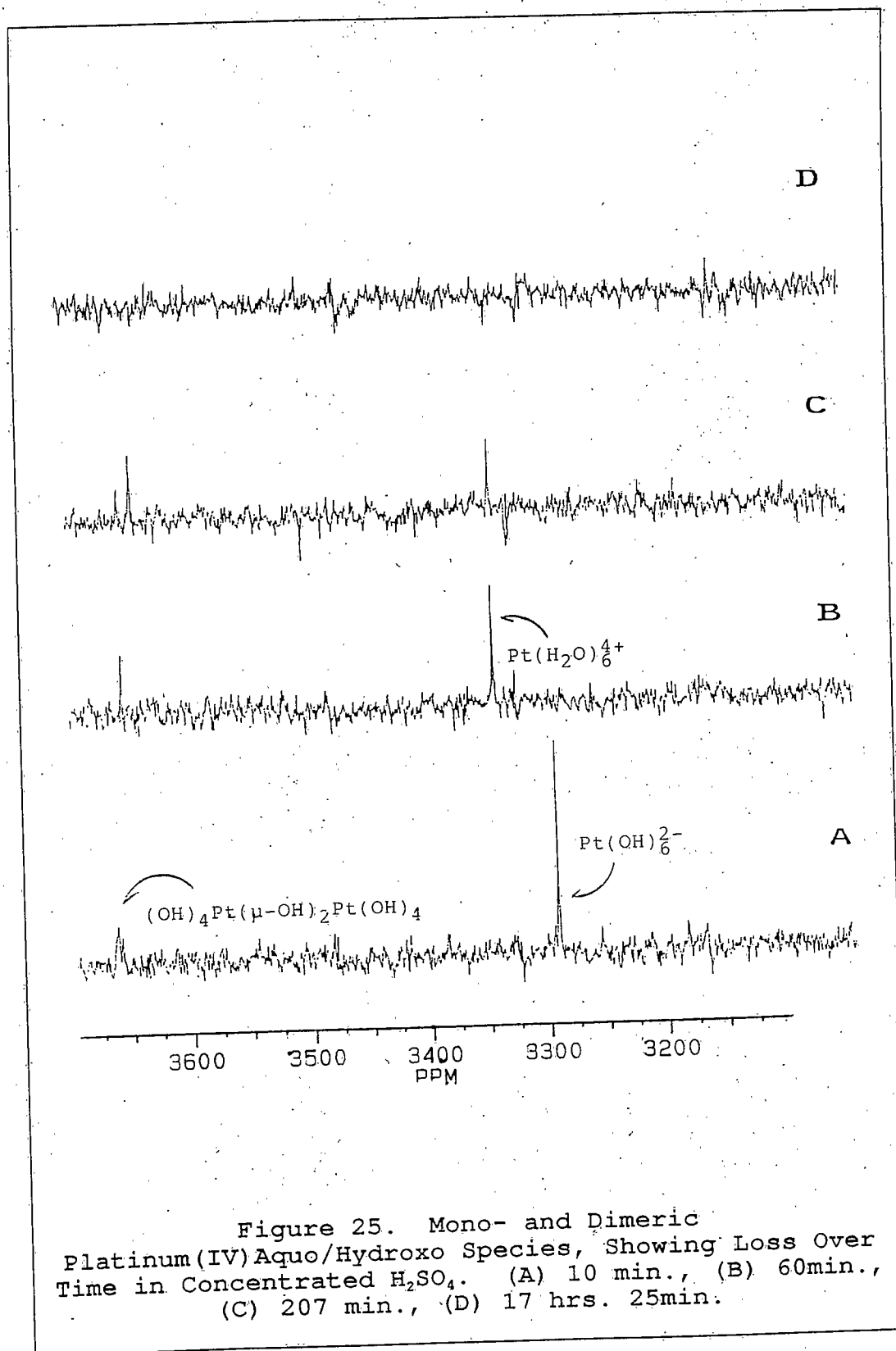
was not acidic enough to dissolve the platinum. At 0.1M acid the platinum dissolved, except for phosphoric acid, and precipitation occurred; for phosphoric acid the acid concentration must be near 1M to obtain a solution. Elevated temperatures caused the rate of precipitation to increase; at 100°C all solids are formed in a minute or less, even at lower acid concentrations. If the acid solution was kept cold in ice while the platinum dissolved, colored solutions were briefly obtained; these solutions had observable ^{195}Pt NMR resonances (see below) which quickly disappeared shortly before precipitation began.

Precipitates all appeared as homogeneous powders, and ranged in color from pale yellow to red-orange. Attempts to grow crystals by reducing reaction rates (lower temperature or concentrations) proved fruitless--either solid still precipitated too quickly for crystal growth, or no solid precipitated at all; layering of acid solutions with organic solvents (acetone, acetonitrile, alcohols), or slow reduction of solution volume by vacuum similarly yielded no crystals.

If we made solutions of $\text{K}_2\text{Pt}(\text{OH})_6$ or platonic acid in 1M NaOH first (in which we know the complex to be stable), and then added concentrated acid, we obtained yellow solutions for nitric acid, and orange solutions for the other acids; nonetheless, precipitates still

formed, but more slowly (one to three days.) The solutions thus obtained before precipitation commenced showed ^{195}Pt NMR resonances at 3307 and 3561ppm (Figure 25B). The former resonance was assigned as the protonated $\text{Pt}(\text{OH})_6^{2-}$ species, due to the proximity to the reported resonance of $\text{Pt}(\text{OH})_6^{2-}$; this downfield shift has frequently been observed by us for species in strongly acid media. The second resonance was that due to $(\text{HO})_4\text{Pt}(\mu\text{-OH})_2\text{Pt}(\text{OH})_4^{2-}$ (106), which formed in variable yield in preparations of platinic acid (lending some support to the notion that platinic acid is not merely a simple mononuclear compound.)

Comparison of Figures 25A and B tell us something about the effect acidity has on these two compounds; Figure 25A is in 1M NaOH solution, while 25B is after addition of concentrated sulfuric acid; upon addition of the acid there was a brief formation of lightly colored solid, but it redissolved immediately. Note that while the protonated $\text{Pt}(\text{OH})_6^{2-}$ resonance shifted downfield somewhat (up to 40ppm), the dimer resonance did not shift; thus, the monomeric species appeared to be more sensitive to changes in acidity than did the dimer. This was probably due to differences in the ease of protonation of the coordinated hydroxide groups in the two compounds; the coordinated hydroxides of the monomer must be more basic than those of the dimer, for they



appeared to be more easily protonated than the coordinated hydroxides of the dimer.

Loss of Platinum(IV) NMR Resonances

Solutions of platinic acid in acid showed initial ^{195}Pt NMR spectra of the monomeric protonated $\text{Pt}(\text{OH})_6^{2-}$ ion (and dimeric $(\text{OH})_4\text{Pt}(\mu\text{-OH})_2\text{Pt}(\text{OH})_4^{2-}$ ion if present) that lost intensity within a day or two to yield no peaks in any region of the platinum spectrum. Figure 25 shows the progressive loss of the protonated $\text{Pt}(\text{OH})_6^{2-}$ peak in concentrated sulfuric acid. Spectrum A is a mixture of the monomer and dimer in 1M NaOH; the solution was kept cool with ice as concentrated sulfuric acid was added dropwise to bring the pH to approximately zero. Note the rapid loss of the $\text{Pt}(\text{OH})_6^{2-}$ peak, and the less rapid decrease of the dimer peak.

This is bad news. These platinum(IV) complexes in acid appear to behave the same way the decomposition products of the platinum(III) dimers do-- formation of multinuclear molecules whose NMR resonances broaden to the point of being unobservable.

Elemental Analysis

Elemental analysis of the solids obtained from sulfuric and phosphoric acids indicate multiple platinum

atoms per molecule (Table 11.) The ratio of platinum to sulfate was between 3:1 and 5:1 (agreeing well with reports by Ginzburg(95)); and the platinum to phosphate ratio was 12:1; these high platinum to anion ratios indicated that the compounds were composed mostly of platinum and oxygen/hydrogen; no other atoms were present to account for such a large percentage of the mass. Few anions and several platinum atoms suggest widely dispersed charge over a large molecule, as might be expected with a large, extended chain metal oxide. This polymerization is not unusual in metal-oxygen chemistry(73-96).

Table 11. Results of Elemental Analysis of Solids Obtained from Reaction of Platinic Acid with Sulfuric and Phosphoric Acids.

Sample	%Pt	%S	%P	ratio of Pt:anion
H ₂ SO ₄	54.69	1.8	----	5:1
	43.86	2.31	----	3:1
H ₃ PO ₄	48.80	----	0.63	12:1

Solubility

The solids were insoluble in organic solvents, as well as in boiling water and concentrated acid at 110°C-- only hot HCl dissolved the solids, to give an orange solution with a ¹⁹⁵Pt NMR resonance at 0 ppm for PtCl₆²⁻.

Reaction of K₂Pt(OH)₆²⁻ or platinic acid in DMF or DMSO, to which were then added a few drops of concentrat-

ed acid to obtain solutions, behaved no differently than reactions run in water; solids formed at essentially the same rate, having the same color and solubility properties.

As the same results were observed for the reactions run in aqueous and non-aqueous solvents (DMSO, DMF), this suggests that water does not play a role in the polymerization, indicating an intermolecular type of polymerization that no doubt involves dehydration of coordinated hydroxide/oxide to create bridges between atoms.

How can we learn something about the nature of these polymers? Since we know the platinum is present as platinum(IV), perhaps reducing the polymer with formic acid will break it up into small platinum(II) complexes that we can study using NMR spectroscopy. Unfortunately, these reactions provided black solids with no platinum resonances in solution; we could not affect a partial reduction the platinum in the polymer to platinum (II); once reduction began it proceeded all the way to yield only platinum metal.

Oxidation of Platinum(II) to Platinum(IV)

The goal of this group of experiments has been to understand the chemistry of platinum(IV) in acid, and so to find an appropriate starting material with which to form the sulfato- and phosphato- platinum(III) dimers.

The polymerization that the platinic acid compounds seem to undergo in acid is undesirable, for it prevents our observing the changes in the platinum(IV) spectrum, and so at first glance prevents using such compounds as reactants to form the platinum(III) dimers. We want to be able to watch the formation of these dimers in solution using NMR spectroscopy, and the polymerization obscures part of the picture. What other forms of platinum(IV) could be used?

We know that the dimers decompose upon loss of one of the bridging ligands; what if we start with a platinum(IV) species which already has some of the bridging ligands coordinated? For instance, if a platinum(IV) complex with coordinated sulfate and a platinum(II) complex with coordinated sulfate are used, and then are reacted together in concentrated sulfuric acid (to keep the ligand concentration high), perhaps the two compounds will join to form $\text{Pt}_2(\text{SO}_4)_4^{2-}$. We can envision that as a coordinated sulfate on the platinum(II) dissociates, for instance, the dangling end of a sulfate on the platinum(IV) could coordinate, and thus bridge the two metal centers.

How can we make platinum(IV) species with coordinated sulfate? Direct reaction of a platinum(IV) complex with sulfate might work, but the low lability of platinum(IV) will cause problems (in fact this was

observed to be the case in our hands). What if we form sulfato-substituted platinum(II) species, and then oxidize them to platinum(IV)? The chemistry of $\text{Pt}(\text{H}_2\text{O})_4^{2+}$ with ligands like sulfate, phosphate, and nitrate is well understood through ^{195}Pt NMR spectroscopy studies (106), and it should be simple to oxidize the complexes to platinum(IV), and thus trap the coordinated ligands (like sulfate or phosphate) in a substitutionally inert complex to provide a compound we can react with platinum(II) to try and form the platinum(III) dimers.

Chlorine oxidation of transition metal complexes is well known (1), and oxidation of PtCl_4^{2-} with chlorine gas is a facile method of producing PtCl_6^{2-} (109). The mechanism of chlorine oxidation has been determined to involve the coordination of a chlorine molecule to form a Cl-Pt-OH_2 axis perpendicular to the original coordination plane of the platinum(II) (109) (which produces a single chloride coordination), then releasing the remaining chloride into solution.

When a solution of $\text{Pt}(\text{H}_2\text{O})_4^{2+}$ in 1M HClO_4 was bubbled with Cl_2 gas for 30 seconds, the only ^{195}Pt NMR resonance observed fell at zero ppm, corresponding to the PtCl_6^{2-} ion. What if the tetraaquaplatinum(II) ion with substituted sulfate or phosphate were oxidized?-- this should provide new, stable, easily characterized (by NMR spectroscopy) platinum(IV) complexes with

sulfate/phosphate ligands. These compounds would then be part way towards the formation of the platinum(III) dimers we wish to produce by reverse disproportionation.

Oxidation with Cl₂

Solutions of the tetraaquaplatinum(II) ion in 1M perchloric acid, with K₂SO₄ added to provide an equilibrium distribution of species (Figure 26) were bubbled with chlorine gas for thirty seconds at room temperature. The peaks observed in the ¹⁹⁵Pt NMR spectrum for the platinum(II) sulfate substituted complexes disappeared, and four new resonances formed (Figure 27.) The peaks around 2300 ppm must be those for compounds containing two chloride ions due to the much larger shift caused by chloride substitution (about 400 ppm) than for sulfate substitution (about 70 ppm). Similarly, the peaks at 2862 and 3040 ppm represent compounds with one chloride. Note that since the difference in each pair of peaks is about the same, the resonances do not indicate cis/trans isomers with respect to chloride location (the downfield peak has only one chloride!), so the peaks represent compounds differing in the number of substituted sulfates. The downfield peaks are assigned as having one sulfate, and the upfield peaks as having no sulfates (analogous to the platinum(II) peak assignments). These assignments agree well with the reported resonance of PtCl(OH)₅²⁻ at 2840 ppm, and trans-PtCl₂(OH)₄²⁻ at 2208

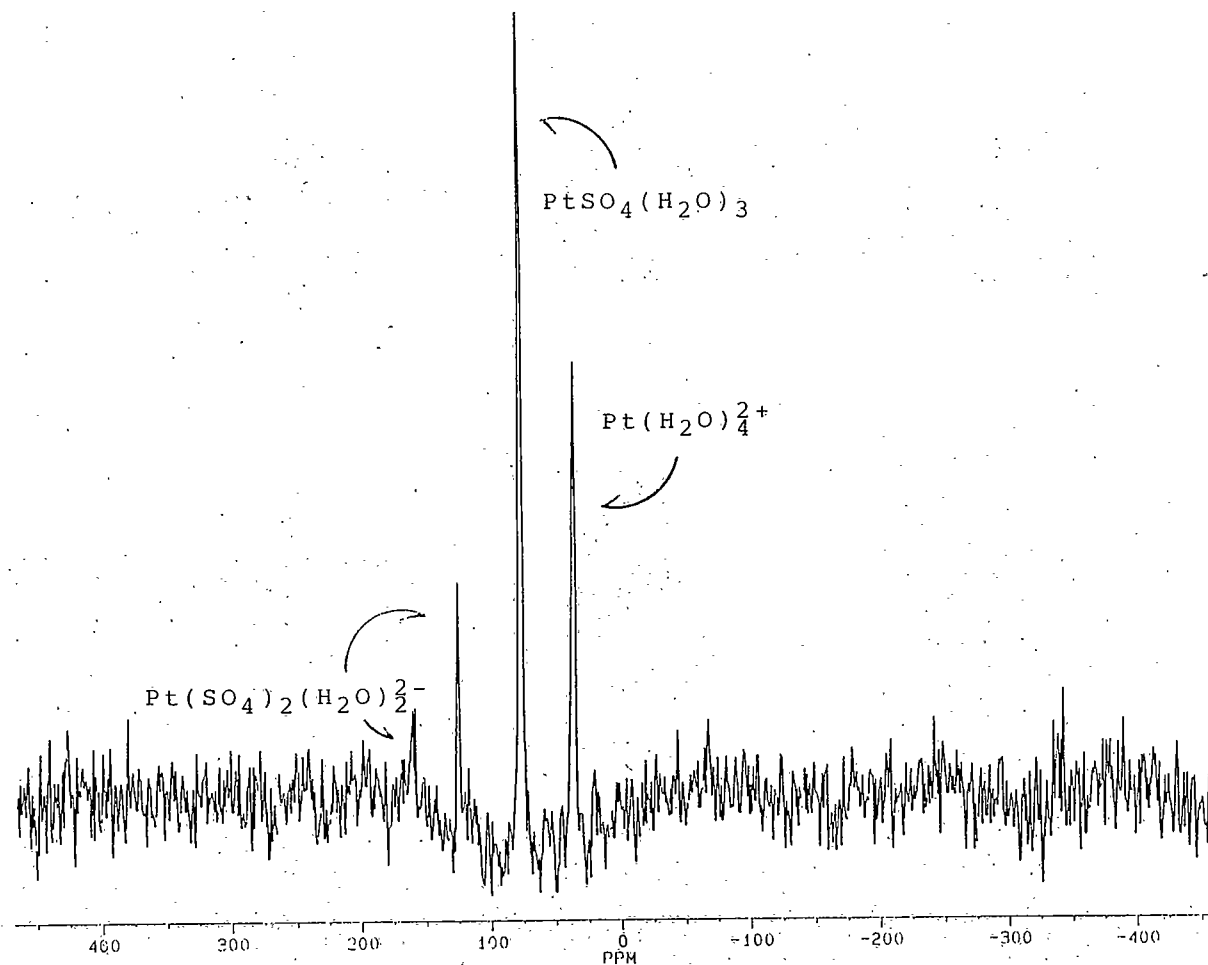


Figure 26. ^{195}Pt NMR Spectrum of Sulfato- Complexes of $\text{Pt}(\text{H}_2\text{O})_4^{2+}$ in 1M HClO_4

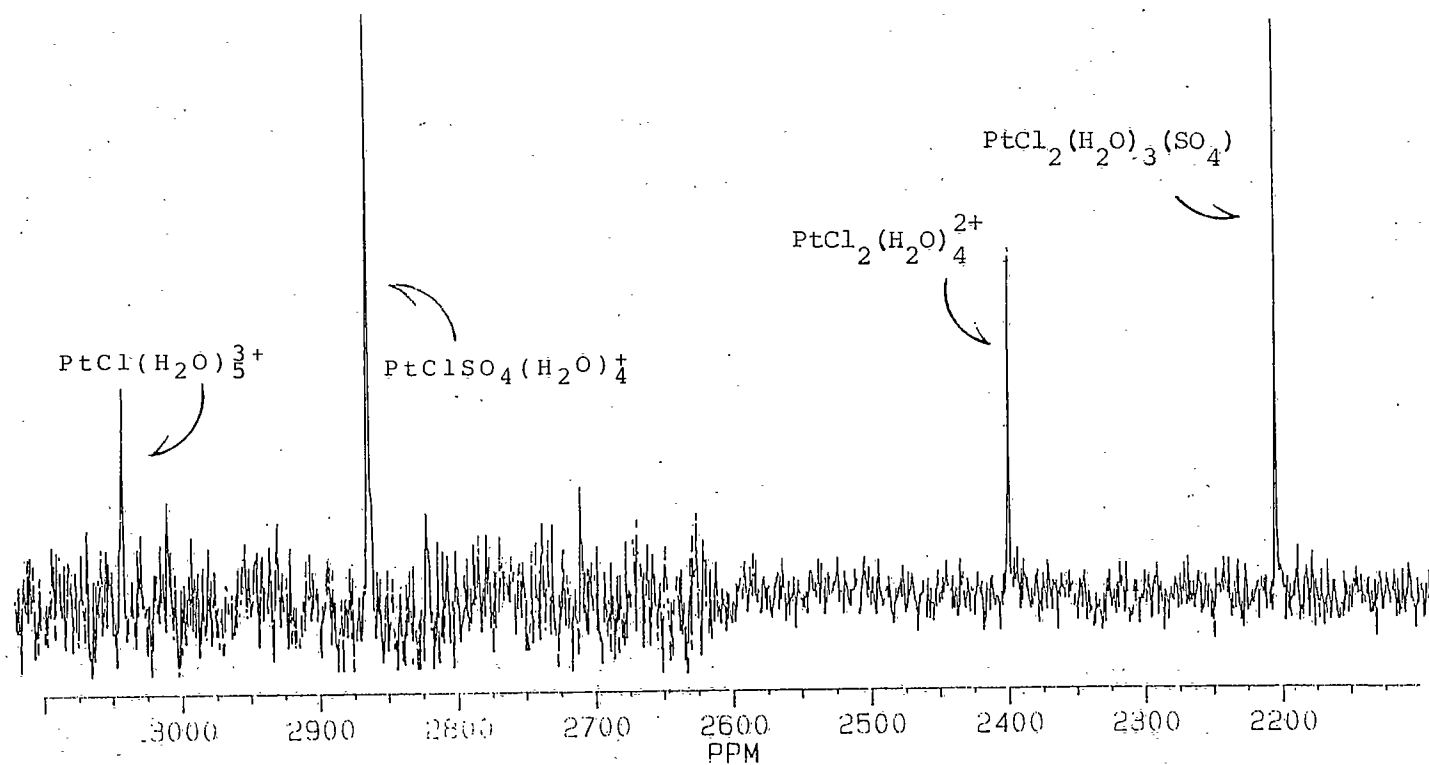


Figure 27. ^{195}Pt NMR Spectrum of Cl_2 Oxidation Products of Sulfato-Complexes of $\text{Pt}(\text{H}_2\text{O})_4^{2+}$ in Dilute H_2SO_4 .

ppm. Note the trend in the shift of the resonances of the complexes in acid solution relative to the resonances in base; in all cases except for hexachloroplatinate(IV), the peaks for the compounds shifted downfield from 14 to 354 ppm (Table 12.) If we compare the relative intensities of the platinum(IV) peaks with the platinum(II) peaks from which they arise, however, the intensities are wrong.

Condit- ion	$\text{Pt}(\text{OH})_6^{2-}$	$\text{PtCl}(\text{OH})_5^{2-}$	$\text{trans-Pt-Cl}_2(\text{OH})_4^{2-}$	
Base	3290ppm	2840	2208	
Acid	3307	3040		

Elding reports only one chloride is added upon oxidation with chlorine gas; the other chloride ion remains in solution. We observe the formation of the monochloro- species, but we also see the formation of dichloro complexes; how does the second chloride coordinate? Once the platinum is oxidized to platinum(IV), the complex should be substitutionally inert, preventing further chloride coordination. There is something unexpected going on here.

Since both mono- and di-chloro species exist after oxidation, we might expect the formation of more dichloro-platinum(IV) than monochloro-platinum(IV); the

dichloro- complex uses up two chlorides for each chlorine molecule, while the monochloro- species has left a chloride ion in solution. This remaining chloride seems to coordinate to the oxidized metal, thus producing more dichloro- complexes than monochloro-. This appears to be the case, judging by the signal to noise ratio of the baseline in the two spectra.

We have a problem; the goal was to make platinum(IV) species with coordinated sulfate (for instance), and one chloride. Instead we formed complexes with more chlorides; the presence of chloride is expected to inhibit dimer formation, for we know that chloride is a strong enough ligand that it prevents the polymerization of the decomposition products of the platinum(III) dimers, and will no doubt similarly prevent the formation of the platinum(III) dimers; for such a strongly coordinating ligand the likelihood of chloride replacement by sulfate or phosphate to form the dimers is small.

What more can we learn about this oxidation? Perhaps a different ligand will behave differently.

Solutions of $\text{Pt}(\text{H}_2\text{O})_4^{2+}$ in 1M perchloric acid with KNO_3 added to form an equilibrium mixture of nitrate-substituted species (Figure 28) were bubbled with chlorine gas for thirty seconds; the platinum(II) peaks disappeared, and several new peaks arose (Figure 29A.)

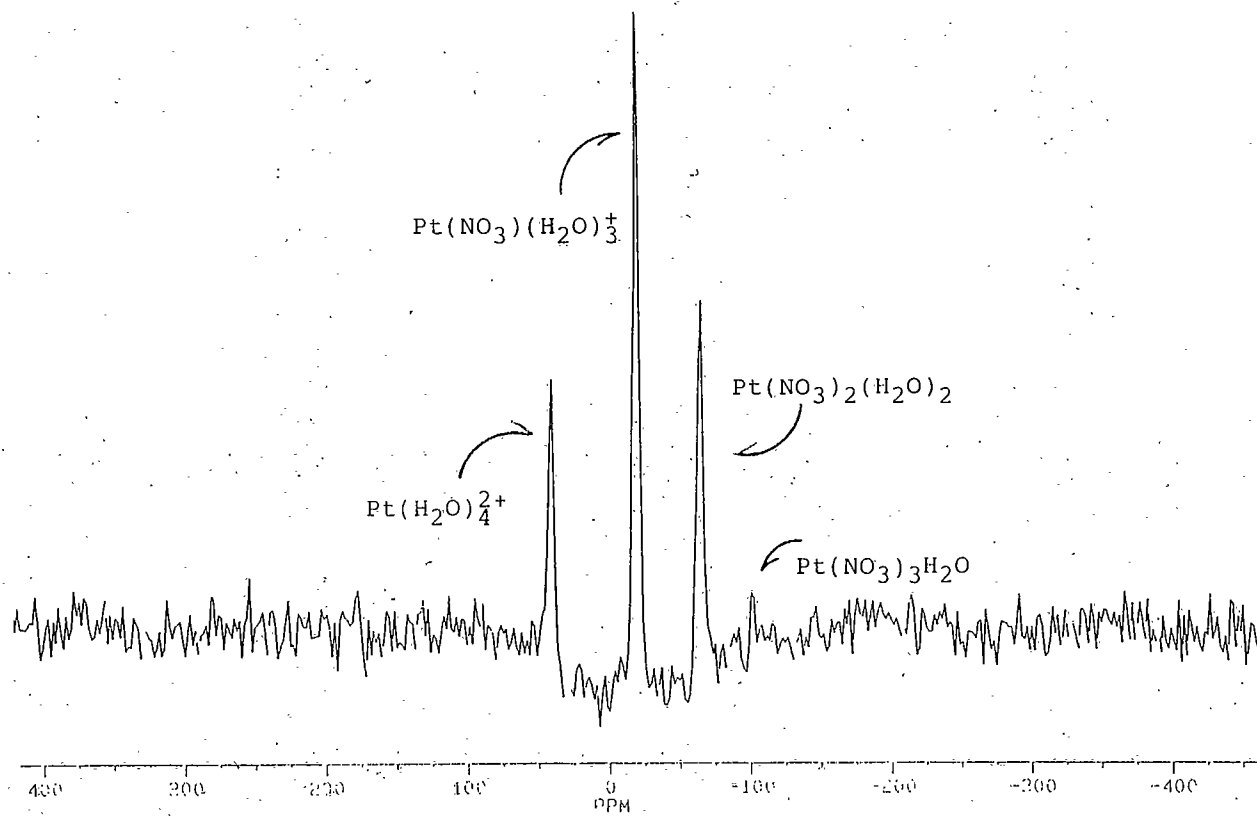


Figure 28. ^{195}Pt NMR Spectrum of Nitrato-Complexes of $\text{Pt}(\text{H}_2\text{O})_4^{2+}$ in 1M HClO_4 .

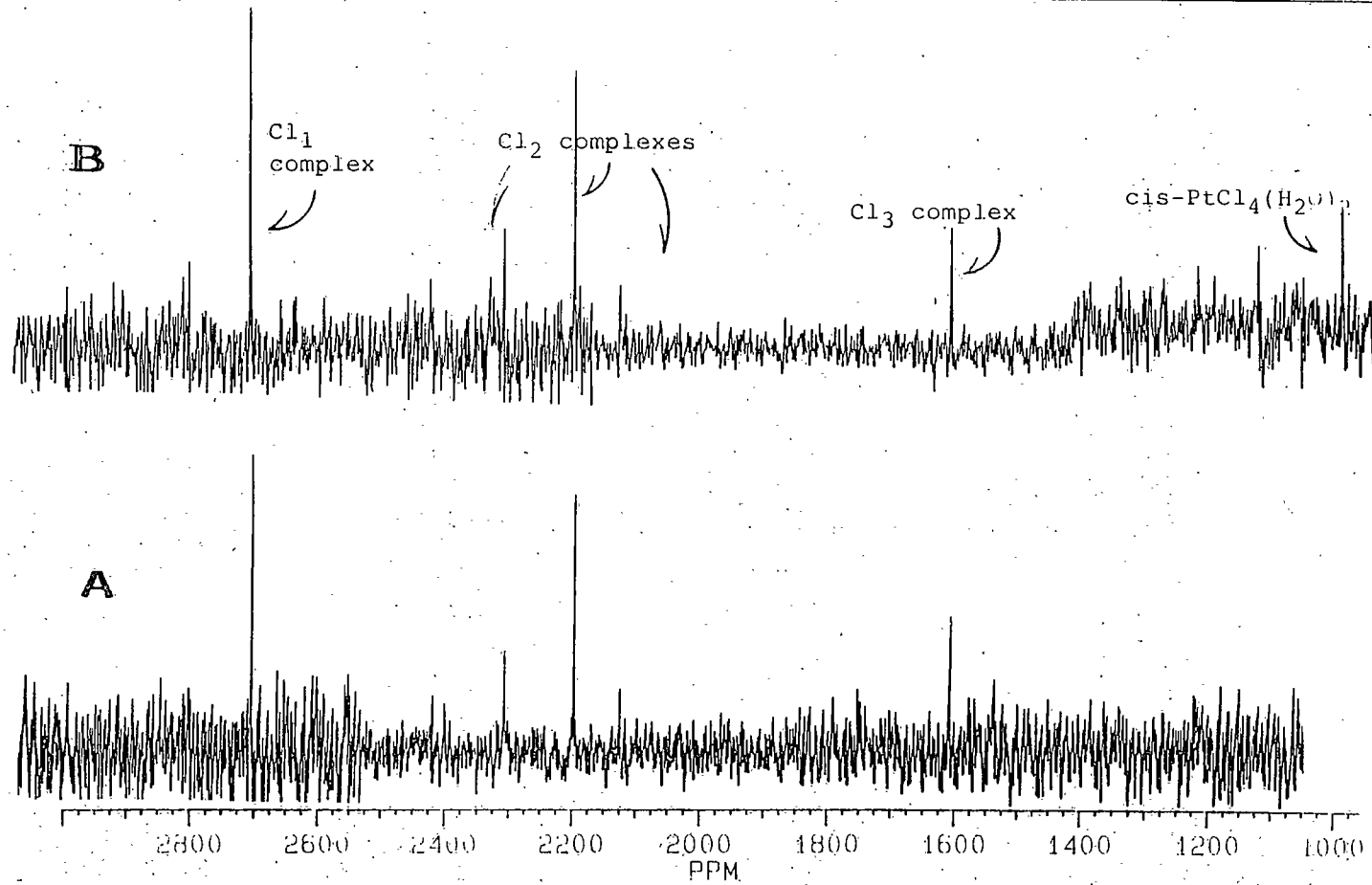


Figure 29. ^{195}Pt NMR Spectrum
of Cl₂ Oxidation Products of Nitrate-Complexes
of Pt(H₂O)₄²⁺. Bottom Day one, Top Day Three.

The resonance at 1607.5 ppm must have three chlorides, the peaks clustered around 2250 ppm must have 2 chlorides, and the 2711 ppm peak one chloride based upon the chemical shift for sequential chloride substitution. Two days later the spectrum in Figure 29B was obtained. A new peak at even higher chloride substitution appeared at 990 ppm (the other new peak at 1121 ppm was a noise spike at 01 due to pulse breakthrough), agreeing with the resonance reported for $\text{cis-PtCl}_4(\text{OH})_2^{2-}$.

In another run of this same reaction, an equilibrium mixture of the nitrate-substituted platinum(II) species (see Figure 28) was bubbled with chlorine gas for 13 minutes and then flushed with nitrogen gas for four minutes to remove excess chlorine; ^{195}Pt NMR spectroscopy gave the spectrum in Figure 30. Note that the intense peaks at 2711, 2199, and 1607 ppm observed in Figure 29A did not appear, but new intense peaks at 2441, 2422, 1741, 1435, and 1278 did appear. These new peaks are difficult to assign to specific compounds as they lie between the reported resonances that we would expect for multiple nitrate substitution of chloro-platinum(IV) species. The peaks around 2450 ppm must have either one or two chlorides; the 1750 ppm peak must have three chlorides; the 1279 ppm peak contains four chlorides; and the resonance at 994 ppm, as observed in Figure 29B, corresponds to $\text{cis-PtCl}_4(\text{H}_2\text{O})_2$.

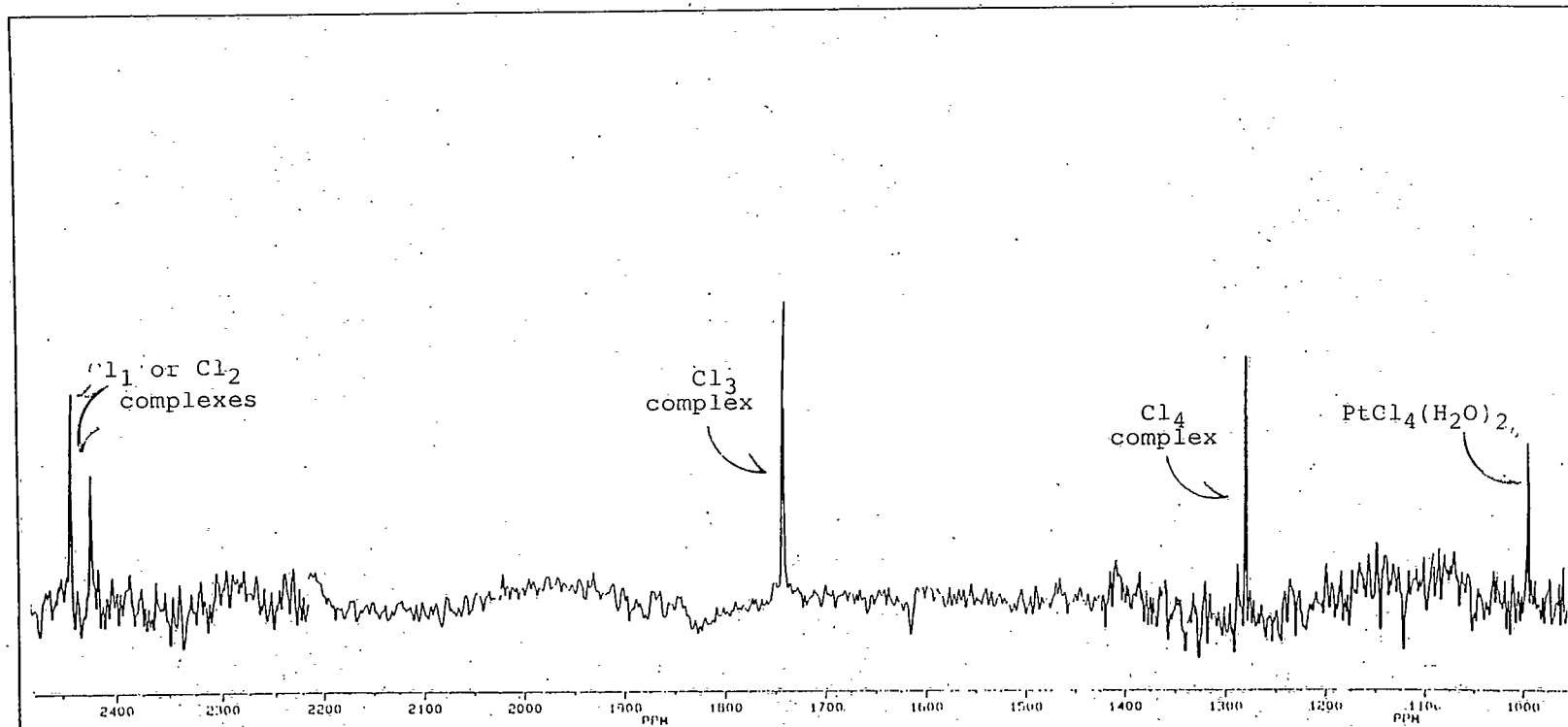


Figure 30. ^{195}Pt NMR Spectrum of Cl₂ Oxidation Products of Nitrate- Complexes of Pt(H₂O)₄²⁺ Bubbled with N₂.

A solution of tetraaquaplatinum in 1M perchloric acid plus monohydrogenphosphate to give the equilibrium distribution of phosphato-substituted species indicated in Figure 31 was bubbled with chlorine gas for 30 seconds; the color changed from green/black to dark red/brown. All platinum(II) peaks in the ^{195}Pt NMR spectra disappeared, and new peaks formed (Figure 32.) Since the platinum(II) resonances shifted about 150 ppm for each coordinated hydrogenphosphate, all that is needed to assign the new peaks is to subtract multiples of about 150 ppm from the chemical shift of each of the resonances until we arrive at a resonance for a known platinum(IV)-chloride compound. In this way we can assign the 1131 peak to $\text{cis-PtCl}_4(\text{HPO}_4)^{2-}$, and the 2212 peak to $\text{fac-Pt}(\text{HPO}_4)_3\text{Cl}_3^{5-}$; the 2424 resonance could arise from either the cis-dichloro complex with two phosphates, or the trans-dichloro complex with one phosphate. Since the pair of peaks at 2660 ppm indicate two species with the same chloride arrangement and different phosphate arrangements, the 2424 ppm resonance must be due to the $\text{trans-Cl}_2\text{HPO}_4\text{Pt}$ compound. The two peaks at 2660 ppm are the trans-dichloro species with two monohydrogenphosphate ions (the shift for the two isomers is the same as in the platinum(II) equilibrium.) Note the similarity between the four most downfield peaks in Figure 32 and the equilibrium distribution of the platinum(II) phosphate

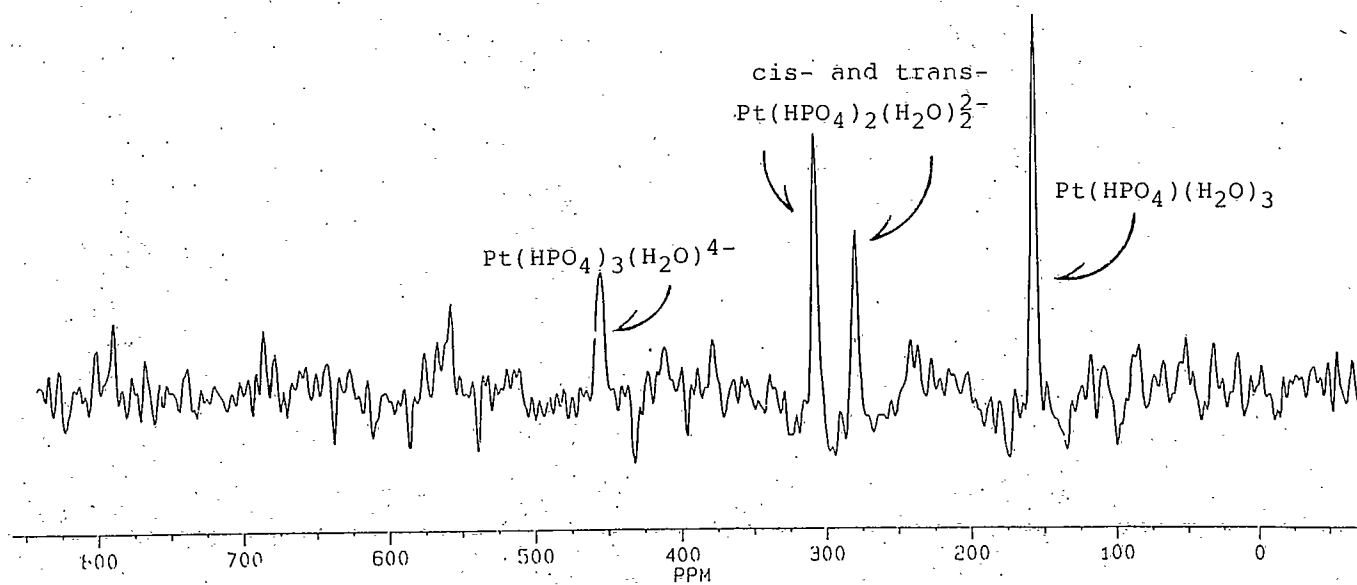


Figure 31. ^{195}Pt NMR Spectrum of Phosphato- Complexes of $\text{Pt}(\text{H}_2\text{O})_4^{2+}$ in 1M HClO_4 .

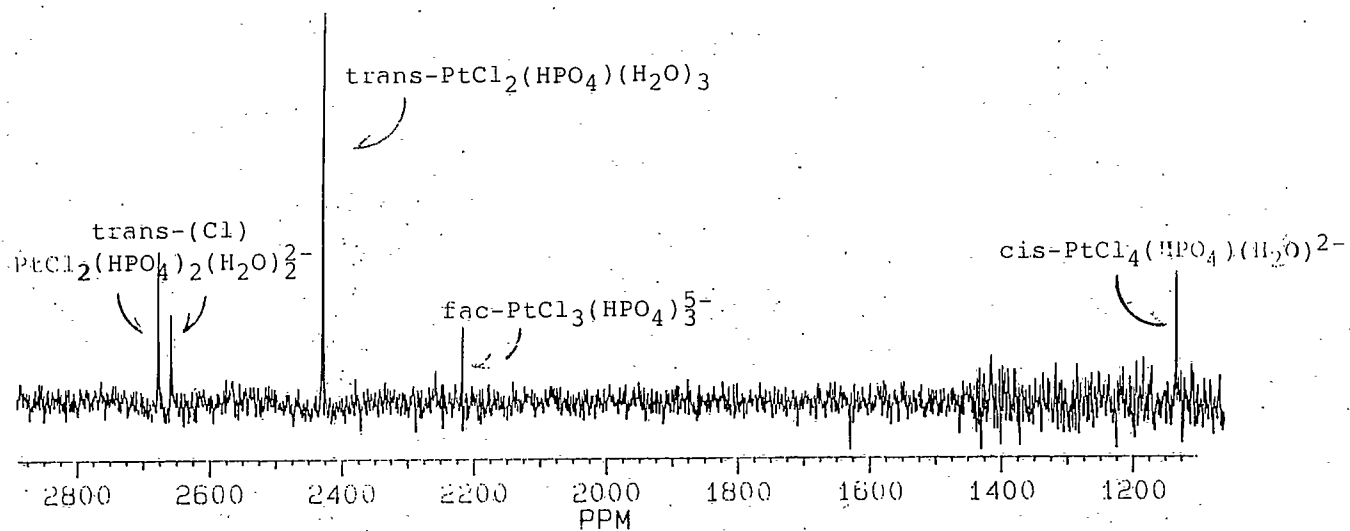


Figure 32. ^{195}Pt NMR Spectrum of Cl_2 Oxidation Products of Phosphato- Complexes of $\text{Pt}(\text{H}_2\text{O})_4^{2+}$.

peaks in Figure 31. The small peak at 2914 in Figure 32 must be due to trans-monochloroplatinum(IV) with three monohydrogenphosphates, in accordance with Figure 31.

Figure 33 shows two weak peaks at 3335 and 3390 ppm; these could be due to $\text{Cl}(\text{HPO}_4)_2\text{Pt}^{-1}$ complexes (note the similarity to Figure 31), but seem shifted too far downfield; the $\text{ClHPO}_4\text{Pt}^+$ peak at around 2800-2900 ppm is also missing. This peak cannot be substituted $\text{Pt}(\text{OH})_6^{2-}$, as the compound must have at least one chloride coordinated to have been oxidized to platinum(IV).

These results were interesting in that they demonstrated the use of chlorine gas as an oxidant to generate new platinum(IV) species (see Table 13), but for our goal the multiple coordination of chloride observed is disappointing. The mixtures of multiple chloro- (up to four chlorides!) substituted sulfato-, nitrate-, and phosphato- platinum complexes suggested that oxidation by Cl_2 of platinum(II) to platinum(IV) may not provide the sort of starting materials wanted to run the reverse disproportionation reactions; while the multiple sulfate, nitrate, and phosphate substitutions are what we were after, the unexpectedly high number of chloride atoms in the compounds will introduce problems in the intended reactions with platinum(II) because of the strong chloride binding to platinum, inhibiting formation of the platinum(III) dimers by reverse disproportionation. What

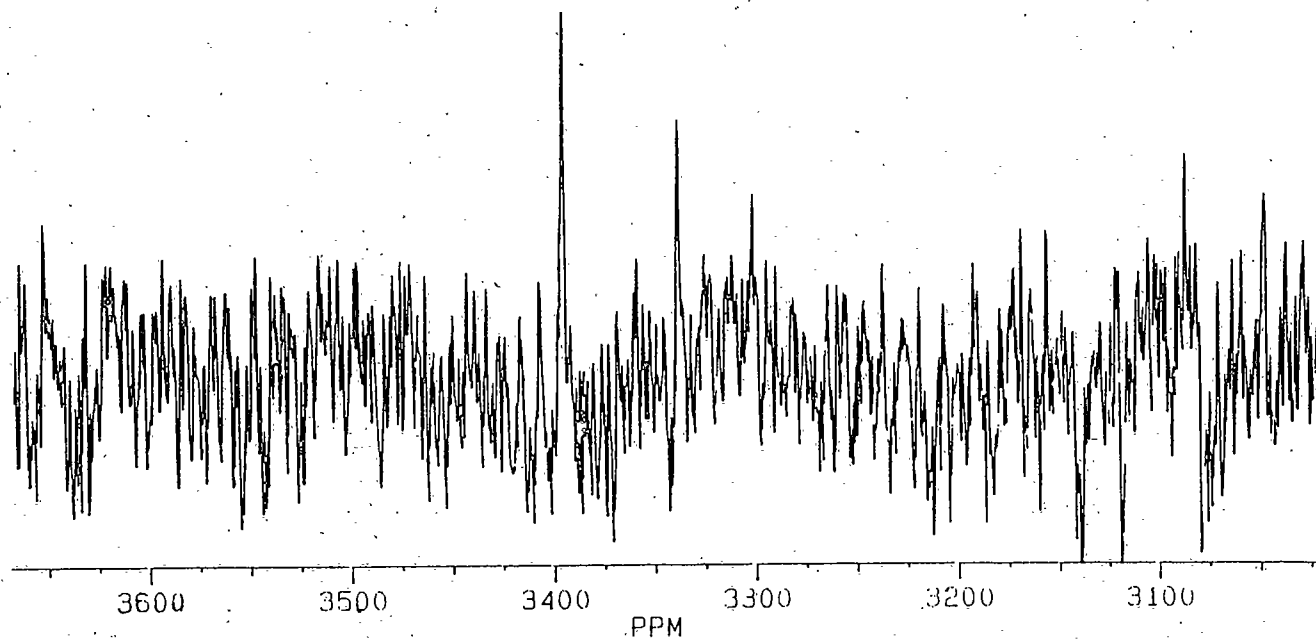


Figure 33. ^{195}Pt NMR Spectrum of Cl_2
Oxidation Products of Phosphato- Complexes of $\text{Pt}(\text{H}_2\text{O})_4^{2+}$.

if other, non-coordinating oxidizing agents are used?

Table 13. ^{195}Pt NMR Chemical Shifts of Products of Cl_2 Oxidation of Platinum(II) Complexes.		
Anion	Compound	Chemical Shift (ppm)
SO_4^{2-}	$\text{PtCl}_2(\text{H}_2\text{O})_{42+}$	2198
	$\text{PtCl}_2\text{SO}_4(\text{H}_2\text{O})_3$	2395
	$\text{PtClSO}_4(\text{H}_2\text{O})_4^+$	2862
	$\text{PtCl}(\text{H}_2\text{O})_5^{3+}$	3040
NO_3^-	$\text{cis-PtCl}_4(\text{H}_2\text{O})_2^{2-}$	990
	species w/ 4 Cl^-	1279
	species w/ 3 or 4 chlorides	1435
	species w/ 3 Cl^-	1608
	species w/ 3 Cl^-	1741
	species w/ 2 Cl^-	2199
	species w/ 2 Cl^-	2309
	species w/ 1 or 2 chlorides	2422
	species w/ 1 or 2 chlorides	2441
species w/ 1 Cl^-	2711	
HPO_4^{2-}	$\text{cis-PtCl}_4\text{HPO}_4\text{H}_2\text{O}^{2-}$	1131
	$\text{fac-PtCl}_3(\text{HPO}_4)_3^{5-}$	2212
	$\text{trans-PtCl}_2\text{HPO}_4(\text{H}_2\text{O})_3$	2424
	$\text{trans}(\text{Cl})-\text{PtCl}_2$ cis- and trans- $(\text{HPO}_4)_2(\text{H}_2\text{O})_2^{2-}$	2652 2673
	$\text{trans-PtCl}(\text{HPO}_4)_3^-$ $(\text{H}_2\text{O})_2^{3-}$	2914
	?	3335, 3390

Oxidation with Permanganate

Potassium permanganate could be a very useful agent for our needs, for it is a quite strong oxidizer, and the products of the oxidation should not coordinate to the platinum. By reacting the 'bare' $\text{Pt}(\text{H}_2\text{O})_4^{2+}$ ion (i.e., with no other coordinated ligands) with MnO_4^- , we can test the facility of the oxidation.

Solutions of the tetraaquaplatinum(II) ion in 1M perchloric acid to which was added one electron equivalent of KMnO_4 turned brown; NaOH was added to adjust the pH to greater than 12 to precipitate the manganese and stabilize $\text{Pt}(\text{OH})_6^{2-}$, if formed. The ^{195}Pt NMR spectra showed no platinum(II) peaks, and one peak at 3283 ppm, corresponding to $\text{Pt}(\text{OH})_6^{2-}$. The oxidation works!

Now to a solution of partially equilibrated platinum(II) in 1M perchloric acid with sulfate (Figure 34) was added one electron equivalent of KMnO_4 ; MnO_2 precipitated upon addition of 12 drops of 50% NaOH to bring the pH to about 13. This solid was filtered off to leave a green solution, which was condensed and the NMR spectrum collected (Figure 35.) The strong peak at 3249 ppm is probably due to $\text{Pt}(\text{OH})_5(\text{SO}_4)^{3-}$. This resonance is shifted in a different direction from what would be expected from the platinum(II) in acid, because this solution is highly basic, and the direction of the shift is expected to be upfield (we will see that increasing

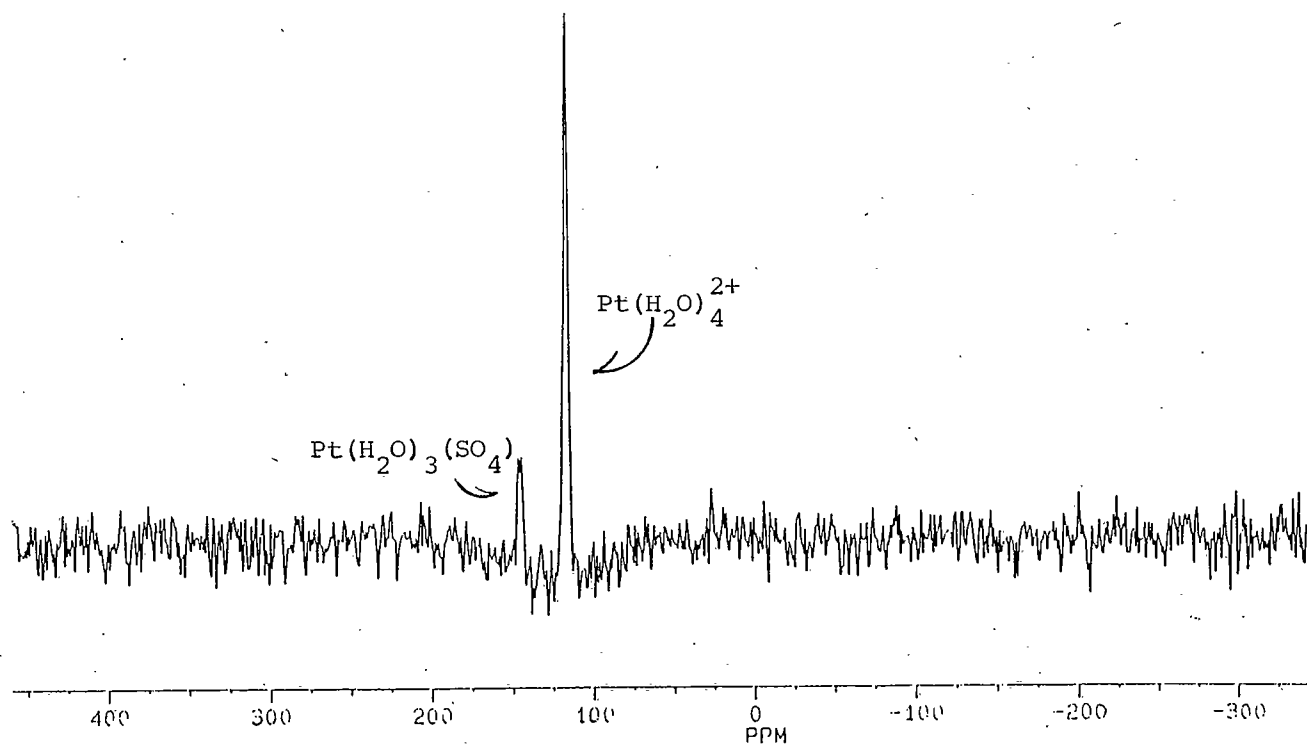


Figure 34. ^{195}Pt NMR Spectrum of Partially Equilibrated sulfato- Complexes of $\text{Pt}(\text{H}_2\text{O})_4^{2+}$ in 1M HClO_4 .

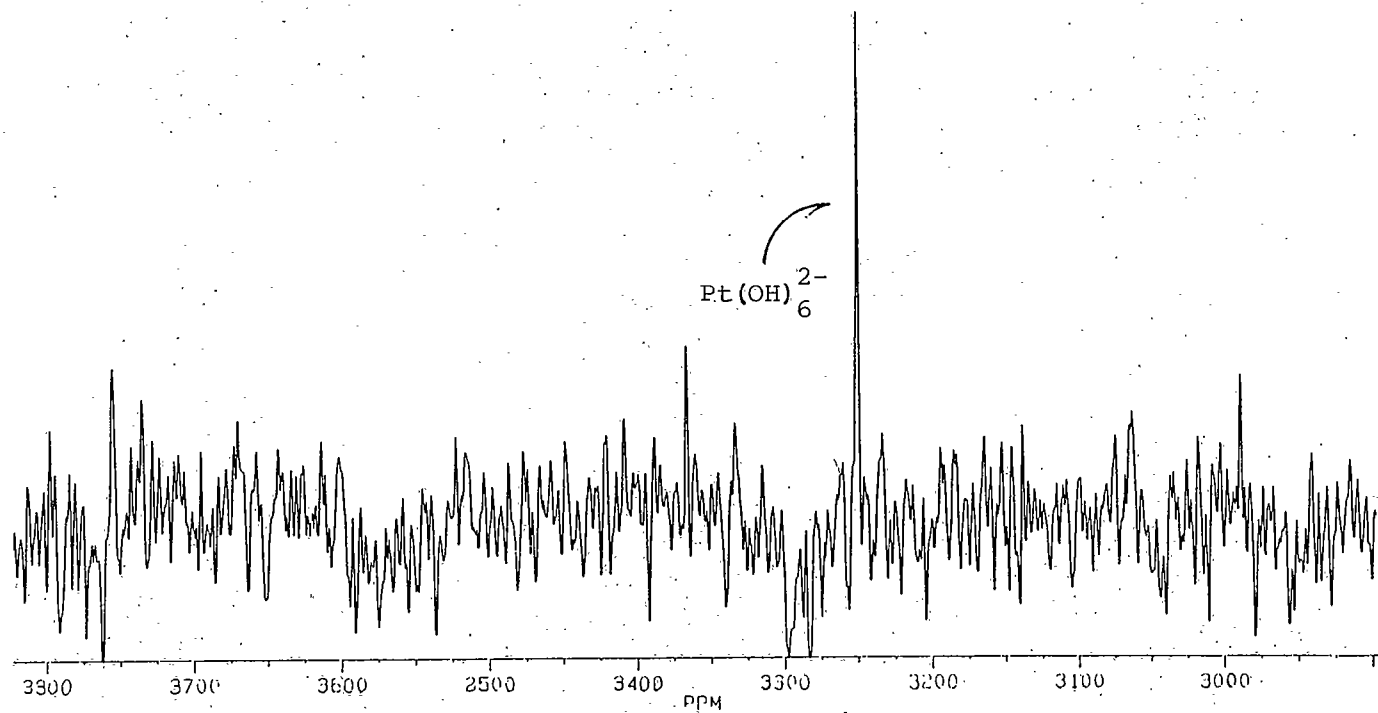


Figure 35. ^{195}Pt NMR Spectrum of MnO_4^-
Oxidation Products of Sulfato- Complexes of $\text{Pt}(\text{H}_2\text{O})_4^{2+}$.

acidity induces downfield shifts, so increasing basicity would be expected to shift resonances upfield.)

For an equilibrated solution of platinum(II) in nitrate/perchloric acid (Figure 36), one electron equivalent of KMnO_4 dissolved in water was added; 50% NaOH was added to precipitate the manganese, and the solid filtered off to leave a yellow/brown solution. This solution was condensed, D_2O added, and the NMR spectrum collected (Figure 37.) The weak peak at 3224 ppm falls very near the peak observed in the sulfate case, and so is assigned to $\text{Pt}(\text{OH})_5\text{NO}_3^{2-}$. Note that this assignment is consistent with the direction of chemical shifts for sulfate and nitrate substitution in the platinum(II) complexes-- sulfate coordination induces downfield shifts, while nitrate causes upfield shifts, consistent with the assigned chemical shifts of the $\text{Pt}(\text{OH})_5\text{SO}_4^{3-}$ and $\text{Pt}(\text{OH})_5\text{NO}_3^{2-}$ complexes.

While permanganate appears to be a useful oxidizing agent for conversion of platinum(II) to platinum(IV) (see Table 14 for resonances of new compounds), the lack of reference compounds (like those used to help assign the resonances to Cl_2 oxidation products) prevented sure resonances assignments to some of the resulting MnO_4^- oxidation products. This inability to identify compounds seems to preclude this method for the search for formation of platinum(IV) starting materials for reverse

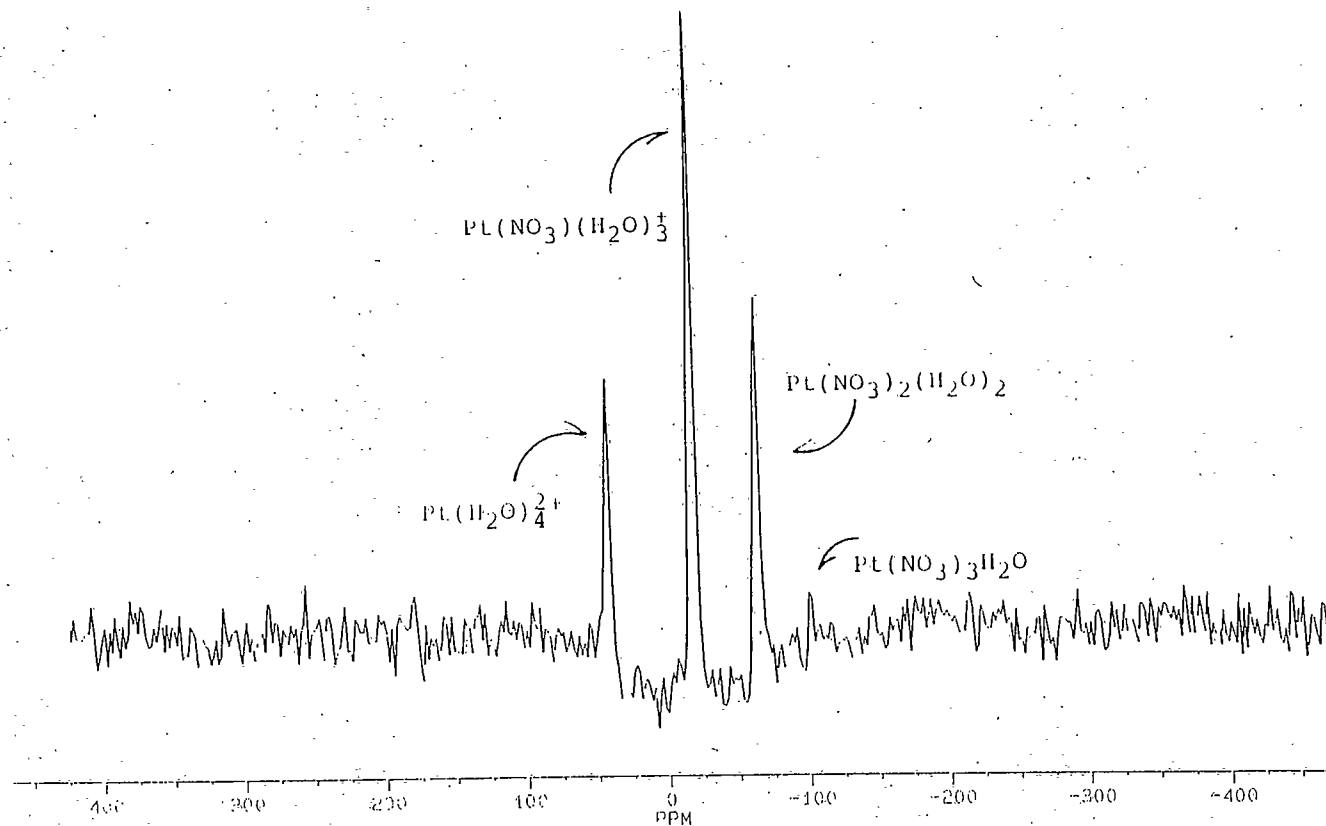


Figure 36. ^{195}Pt NMR Spectrum of Nitrate- Complexes of $\text{Pt}(\text{H}_2\text{O})_4^{2+}$ in 1M HClO_4 .

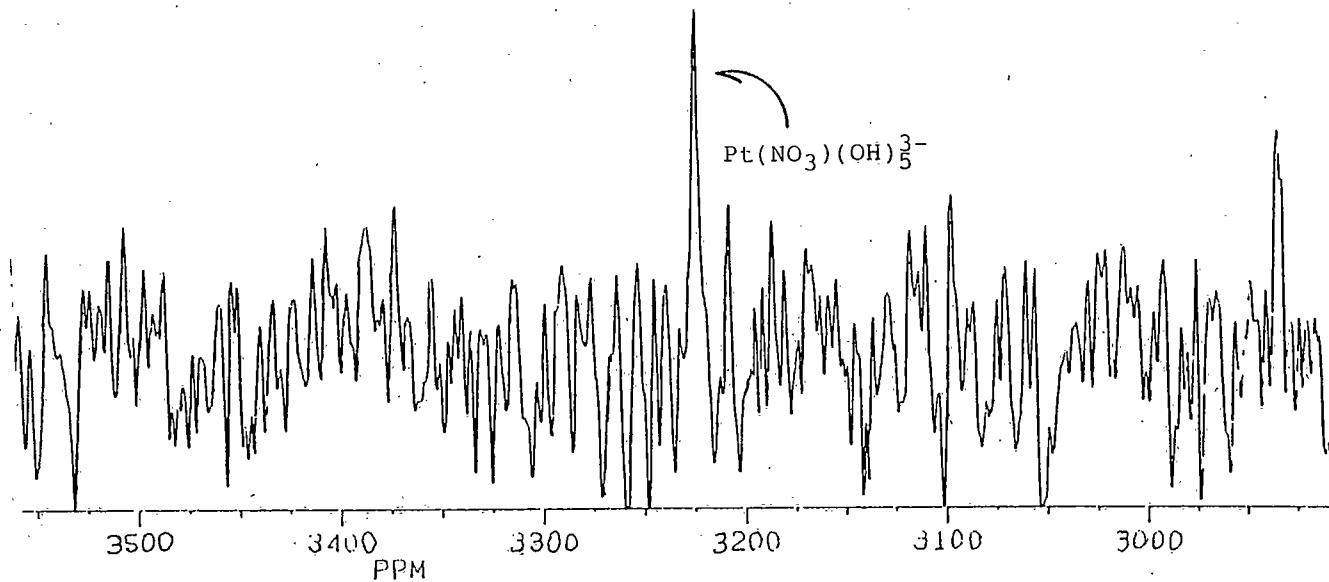


Figure 37. ^{195}Pt NMR Spectrum of MnO_4^-
Oxidation Products of Nitrate- Complexes of $\text{Pt}(\text{H}_2\text{O})_4^{2+}$ in Base.

disproportionation.

Table 14. ^{195}Pt NMR Chemical Shifts of Complexes Formed by Permanganate Oxidation of Platinum(II) Species.		
Anion	Compound	Chemical Shift (ppm)
SO_4^{2-}	$\text{Pt}(\text{H}_2\text{O})_5\text{SO}_4^{2+}$	3249
	$\text{Pt}(\text{H}_2\text{O})_4(\text{SO}_4)_2$	3366
NO_3^-	$\text{Pt}(\text{H}_2\text{O})_5\text{NO}_3^{3+}$	3224

It begins to appear as if the oxidation of platinum(II) species to platinum(IV) will leave us with complicated mixtures of compounds, instead of the simple one or two complexes with bridgeable ligands we had hoped for. Perhaps oxidation with a compound that provides a bridging ligand might be of use; for example, the peroxydisulfate ion will oxidize the platinum, and in so doing provide a ligand we wish to coordinate, sulfate.

Oxidation with Peroxydisulfate

By oxidizing with peroxydisulfate, the product will contain sulfate ion due to attack of the sulfate radical(110) this would be especially convenient for reactions with sulfate, for the oxidation itself would introduce the desired coordinated ligand. It could also provide a means to form mixed bridged dimers, such as sulfate and phosphate.

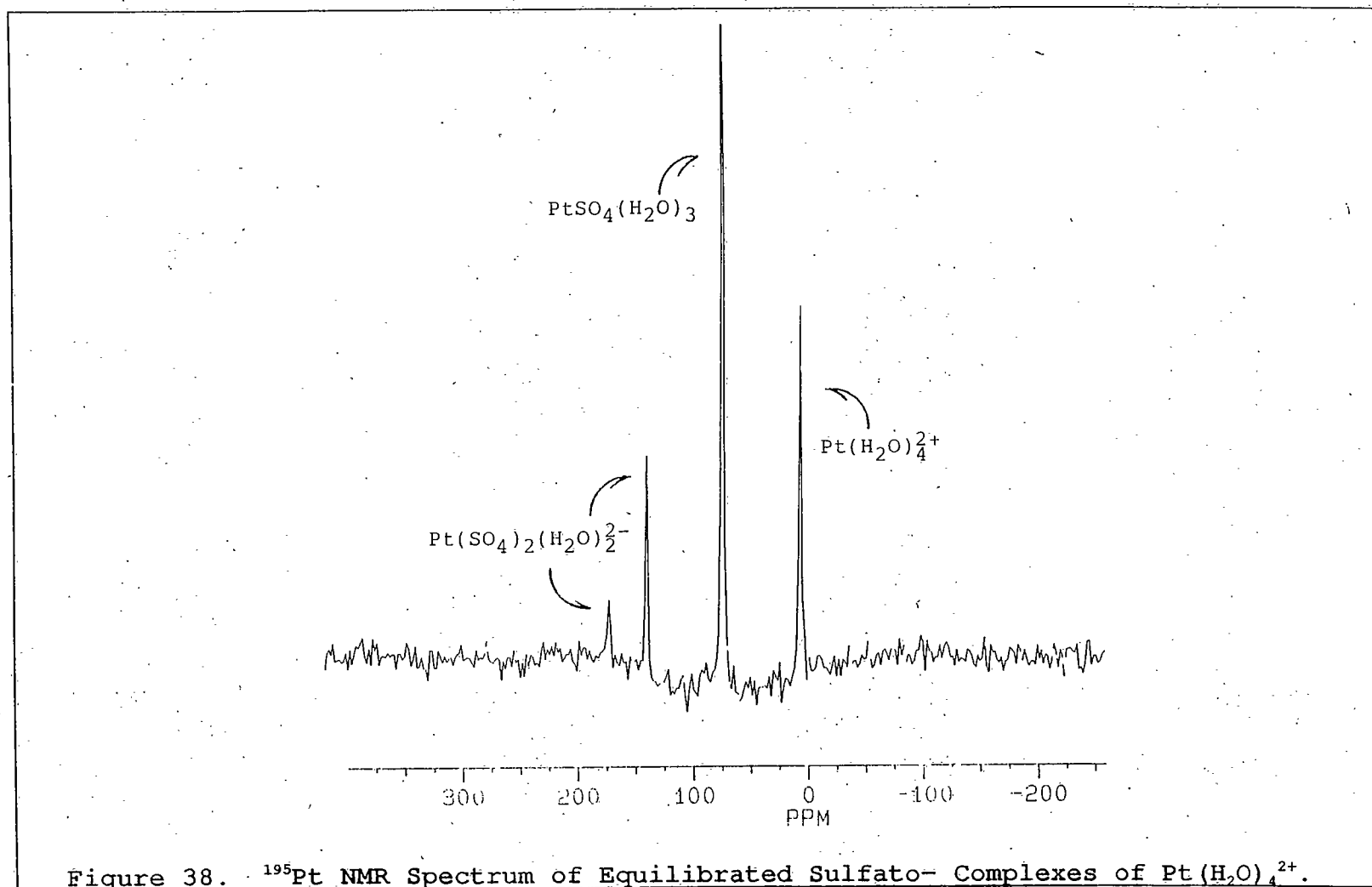
We would now expect that reaction with $\text{S}_2\text{O}_8^{2-}$ in

sulfate solution would also produce polymerization; the same results were obtained when a solution of the tetraaquaplatinum(II) ion in 1M perchloric acid was oxidized with peroxydisulfate; the single resonance of the tetraaquaplatinum(II) ion decreased, while no new resonances were observed.

Here we see the polymerization occurs even in the near absence of bridging ligand (the only sulfate present is due to that from $(\text{SO}_4)_2^{2-}$.) It seems, therefore, that the polymerization is affected only by the coordinated oxygen ligands and the high acidity, and does not require sulfate (or phosphate) coordination to occur.

One electron equivalent of $\text{K}_2(\text{SO}_4)_2$ was added to an equilibrated solution of tetraaquaplatinum(II) ion in sulfate/perchloric acid (Figure 38.) No new peaks were observed in the ^{195}Pt NMR spectrum; a change in the platinum(II) spectrum after 90 minutes was observed, however (Figure 39.) Loss of the more highly substituted species indicates that oxidation occurred; no platinum(IV) resonances were observed, however. The oxidized species must react directly to form the polymerized species believed to exist in other solutions of platinum(IV) in acid.

No polymerization was observed for the Cl_2 oxidations because chloride ion is too good a ligand and prevents polymerization; no polymerization was observed



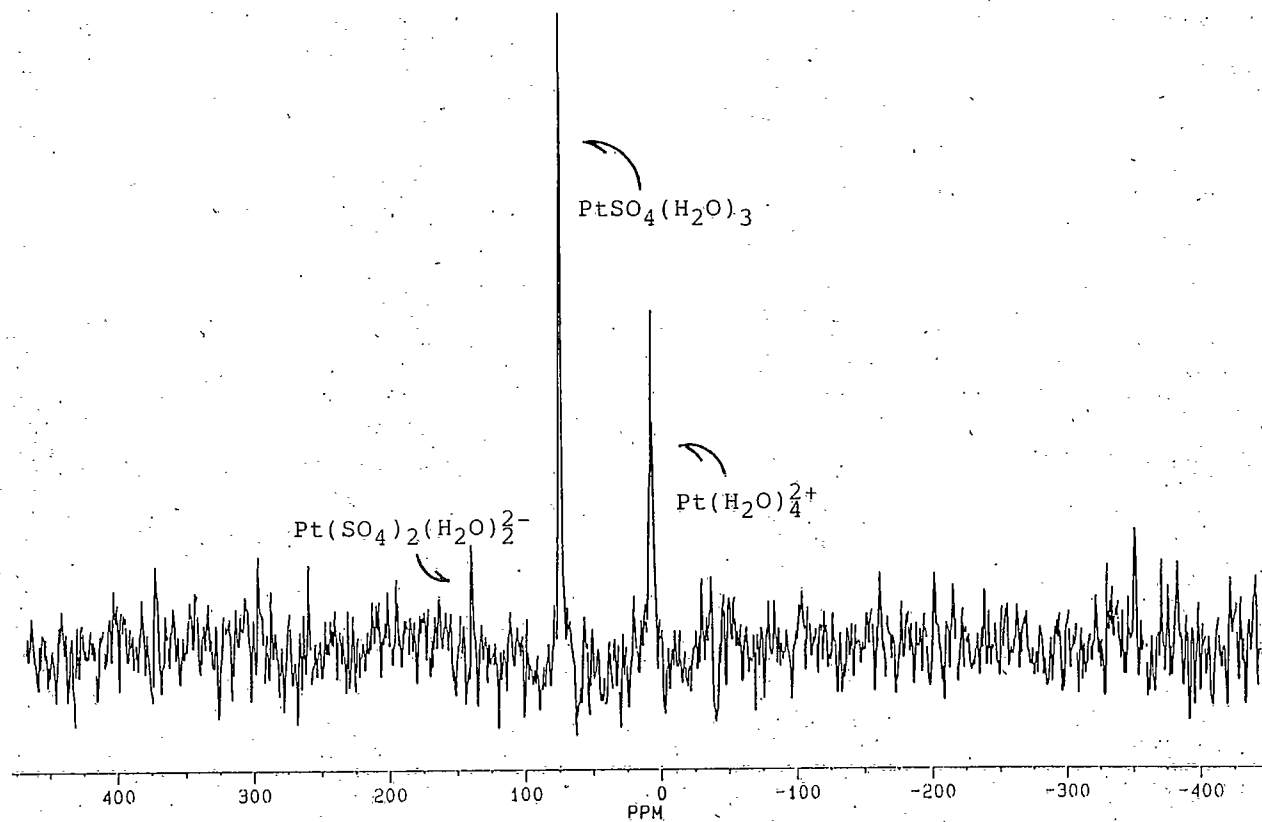


Figure 39. ^{195}Pt NMR of Peroxydisulfate Oxidation Products of Sulfato-Complexes of $\text{Pt}(\text{H}_2\text{O})_4^{2+}$.

for permanganate oxidation because the solutions were basic, a condition under which the platinum(IV) complexes are stable and do not polymerize.

Oxidation with Hydrogen Peroxide

As a final try hydrogen peroxide was used to attempt oxidation. Hydrogen peroxide oxidations yielded the same results as were observed for peroxydisulfate oxidations, with the additional complications that the reduction of hydrogen peroxide seems to form fairly long lived paramagnetic species which broaden all resonances so as to make them unobservable for several hours after addition of peroxide; spectra obtained after these species dissipated showed the same lack of platinum(IV) resonances after oxidation. Additionally, hydrogen peroxide decomposition appeared to produce non-stoichiometric amounts of oxidation; sometimes more or less oxidation was observed than for the amount of peroxide added. This might be due to some effect which causes some of the perchlorate in solution to act as an oxidizing agent.

What have we learned? We have used the oxidation (by four different oxidation agents) of platinum(II) species to prepare several new platinum(IV) complexes, and identified them using ^{195}Pt NMR spectroscopy and a knowledge of how sequential substitution produces

systematic chemical shifts of resonances.

It seems, however, that we will be unable to get a stable, well characterized platinum(IV) species with which to run the reverse disproportionation reactions in acid without the complications of strongly coordinating ligands, or complex mixtures of compounds. With this in mind, perhaps the formation of the platinum(III) dimers by reverse disproportionation will work using the unseen platinum(IV) polymer as the source of the platinum(IV); it may be that by adding the tetraaquaplatinum(II) derived platinum(II) compounds to these acidic solutions of platinum(IV), we may observe NMR resonances corresponding to the platinum(III) sulfate and phosphate dimers.

Platinum(II) in Acid

Previous Work

Now what platinum(II) species might we use to react with the platinum(IV) polymer for reverse disproportionation? Fortunately, much of this work has been done; the paper published by Appleton and Hall (106) completely detailed the reactions and ^{195}Pt NMR resonances of the $\text{Pt}(\text{H}_2\text{O})_4^{2+}$ ion with nitrate, sulfate, phosphate, acetate, and chloride ions in solutions of 1M perchloric acid (Table 15). All reactions in our hands agreed well with these reports. It should be noted that in the case

of the phosphate and acetate substituted species, the pH must be raised to greater than 1.5 to allow complex formation, and then re-acidified to observe sharp resonances (if not re-acidified, the resonances are quite broad.)

Table 15. ¹⁹⁵ Pt NMR Chemical Shifts of Nitrate, Sulfate, Phosphate, Acetate, and Chloride Complexes of Pt(H ₂ O) ₄ ²⁺ . **				
Anion	Mono-complex	Bis-complexes	Tris-complex	tetra-kis-complex
NO ₃ ⁻	-24ppm	-57ppm -59	-96ppm	---
SO ₄ ²⁻	74	133 164	---	---
H ₂ PO ₄ ⁻	145	267 292	424	602
CH ₃ COO ⁻	-20	---	---	---
Cl ⁻	-350	-811 -644	-1185	-1625

It seems that any of these compounds might reasonably be used as the source of platinum(II) in the proposed synthesis of Pt₂(SO₄)₄²⁻ and Pt₂(HPO₄)₄²⁻ by reverse disproportionation.

Reactions in Concentrated Acids

If we are to try and produce the platinum(III) dimers by reverse disproportionation, a first guess at the conditions to use would be the conditions under which the compounds were originally prepared, i.e., strong

acid-- concentrated H_2SO_4 and 50% H_3PO_4 . As we have already observed a shift in the resonances of the platinum(IV) species with changes in acidity, it is prudent to study how the known resonances of the substituted platinum(II) complexes reported above shift in these strongly acidic media.

In addition to the shift in resonances due to acidity, we also found that when $\text{Pt}(\text{H}_2\text{O})_4^{2+}$ was dissolved in concentrated acids, in some cases higher substitutions occurred than had been reported; in every case, however, resonances were shifted downfield by as much as 329 ppm, depending upon the acidity of the solution.

Sulfuric Acid

Addition of one mL of concentrated sulfuric acid to the neutral solid precipitated with 1 M NaOH from 100 mL of a stock solution of 0.01 M $\text{Pt}(\text{H}_2\text{O})_4^{2+}$ in 1 M perchloric acid (approximately 75 mg) caused the resulting solution to become hot; this solution was transferred to an NMR tube and a D_2O insert added, and the ^{195}Pt NMR spectrum collected (Figure 40.) Note the downfield shift of the resonances from their location in 1 M perchloric acid (244-329 ppm, Table 16). Further note the formation of one new species at 629 ppm, assigned to the tris-sulfato species. It is surprising that even in concentrated acid, the $\text{Pt}(\text{H}_2\text{O})_4^{2+}$ ion still existed.

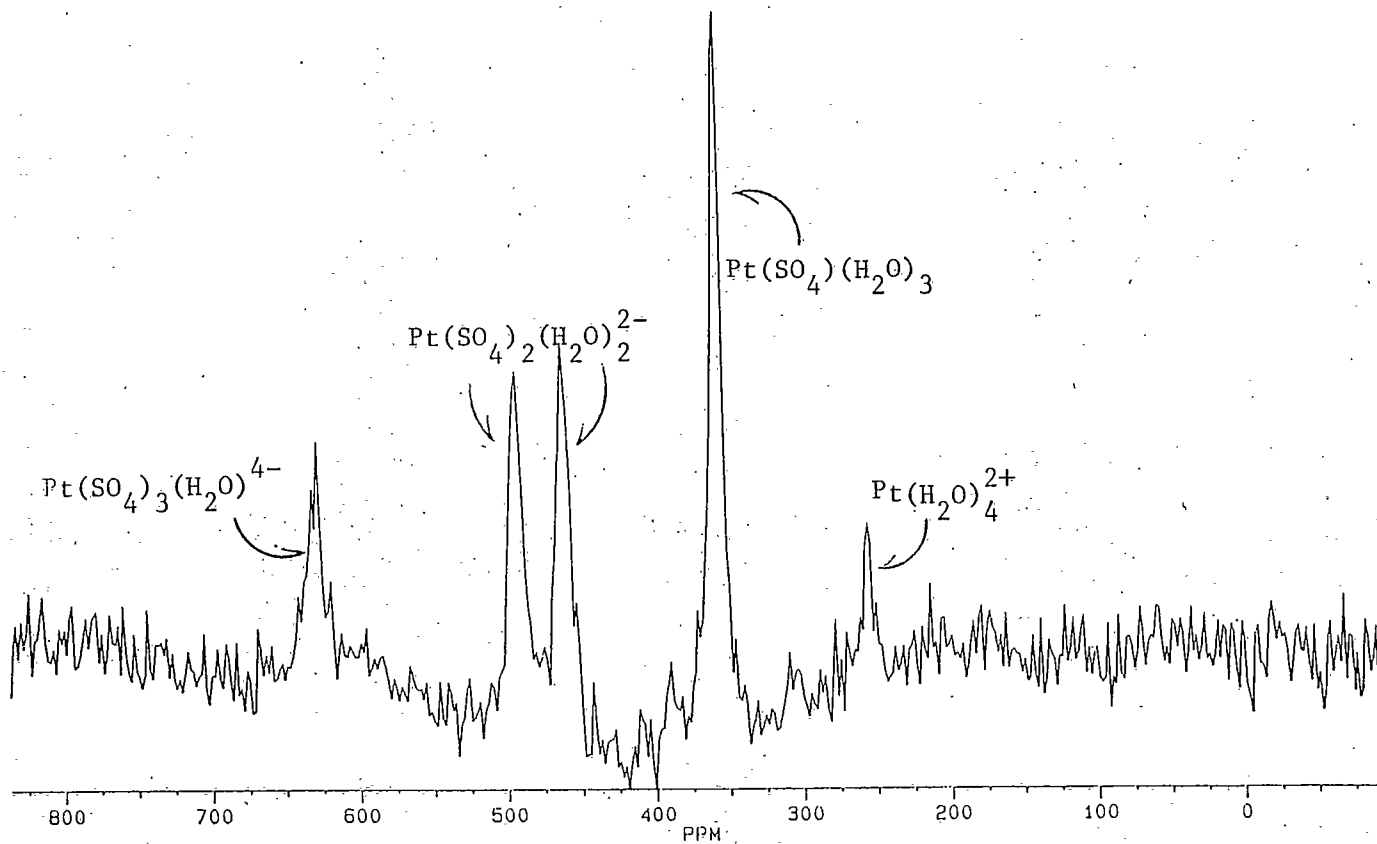


Figure 40. ^{195}Pt NMR Spectrum of Sulfato-Complexes of $\text{Pt}(\text{H}_2\text{O})_4^{2+}$ in Concentrated H_2SO_4 .

Table 16. ^{195}Pt NMR Chemical Shifts of $\text{Pt}(\text{H}_2\text{O})_4^{2+}$ Complexes formed in Dilute and concentrated Sulfate/Sulfuric Acid.				
condi- tions	$\text{Pt}(\text{H}_2\text{O})_4^{2+}$	mono- complex	bis-comp- lexes	tris- complex
>.75M sulfate/ HClO_4	36ppm	74ppm	133ppm 164	----
conc. H_2SO_4	257	357	463 494	629

Phosphoric Acid

Figure 41 shows the neutral $\text{Pt}(\text{H}_2\text{O})_4^{2+}$ solid in concentrated phosphoric acid. No new resonances were observed (all possible coordination sites have been reported), but the tetrakis-substituted species did not appear; the acidity of the platinum atom must be reduced so much in concentrated phosphoric acid with three coordinated hydrogenphosphate ligands that the hydronium ion was a better base and successfully competed with the final hydrogenphosphate to replace the bound water molecule (recall that in 1 M HClO_4 the pH must be increased to 2.5 to allow the more highly substituted species to form.) Note the downfield shift as for the sulfuric acid reaction, but the change is not as large (53-69 ppm, Table 17), no doubt due to the lower acidity of concentrated phosphoric acid compared with sulfuric acid.

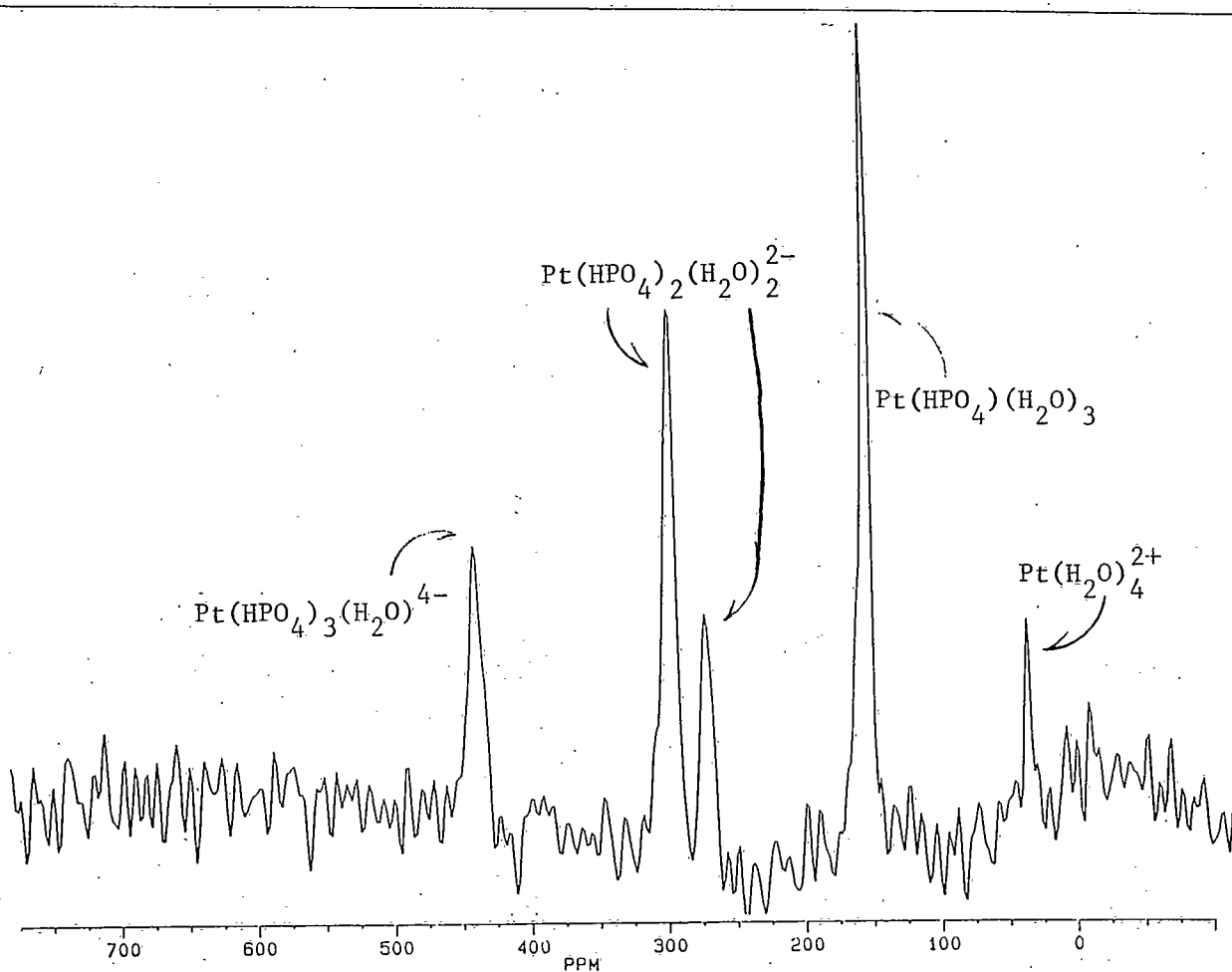


Figure 41. ^{195}Pt NMR Spectrum of Phosphato- Complexes of $\text{Pt}(\text{H}_2\text{O})_4^{2+}$ in Concentrated H_3PO_4 .

Table 17. ^{195}Pt NMR Chemical Shifts of $\text{Pt}(\text{H}_2\text{O})_4^{2+}$ Complexes Formed in Dilute and Concentrated Phosphate/Phosphoric Acid.					
condition	aquo-ion	mono-complex	bis-complex	tris-complex	tetra-comple
$\text{H}_2\text{PO}_4^-/\text{HClO}_4$	36ppm	145ppm	267ppm 292	424ppm	602ppm
50% H_3PO_4	90	208	326 351	493	----

Evidence of Polymerization

Based upon the work discussed earlier by Appleton and Hall, and the reactions described above for the tetraaquaplatinum(II) ion with concentrated sulfuric and phosphoric acids, the platinum(II) ion appears to be well behaved in acidic media. We have observed in two cases, however, indication that platinum(II) chemistry under these conditions can be more complicated.

In an attempt to produce the $\text{Pt}(\text{H}_2\text{O})_4^{2+}$ /perchloric acid stock solution when AgClO_4 was temporarily unavailable, the preparation was conducted in 1M HNO_3 , and the chloride was precipitated with AgNO_3 . The resulting pale green solution showed NMR resonances of the equilibrated nitrate substituted species as reported by Appleton and Hall. In reactions using the solid precipitated from this stock solution with 1M NaOH , it was found that the coordinated nitrate caused undue complications, and the solution remained unused, stored in the refrigerator

under argon. After a year, it was thought the solution could be used in a new series of experiments. The appearance of the solution remained unchanged, with no solids precipitating over time. When attempts were made to precipitate the neutral solid from solution for dissolution at higher concentration for NMR spectroscopy studies, no solid precipitated, even at very high pH (under which conditions the solution turned black and precipitated black solid). The NMR spectra run on a sample of the solution concentrated on a rotary evaporator yielded no NMR resonances in any region of the platinum spectrum; as all the platinum was still in solution, it must have formed some new species.

We might consider two reasons the resonances would be unobserved: either paramagnetic species had formed, or large oligomers formed with many slightly different platinum atoms that broaden the platinum resonances so much they are unobserved. The first case is unlikely, since solutions spiked with known platinum species showed no broadening of those resonances, and since paramagnetic species should interact with light in such a way as to change the color of the solution; no change in color or appearance of the solution occurred. The other explanation, formation of large soluble polymers whose resonances broaden too much to be observed seems a reasonable explanation, as we have already observed this

same effect with platinum(IV) in acid.

The other case in which this behavior was observed was mentioned earlier, in the case where the platinum(III) sulfate dimer was decomposed by Ba^{2+} , or allowed to decompose over time in water, perchloric acid, or sulfate solution. In these instances we saw no formation of the anticipated platinum(II) compounds-- in fact no resonances were observed at all.

It seems that when platinum(II) remains in an acidic solution containing moderately coordinating ligands, over time a slow polymerization may occur which restricts observation of NMR resonances. In the case of the disruption of the dimer, not only were the ligands already coordinated to the metal, but it was also bound to another metal atom as well; one might think of this situation as one in which the polymerization process had already begun, and so it was not surprising that no platinum(II) resonances were observed in these reactions.

Reverse Disproportionation Reactions

We may now have enough information to try and form the platinum(III) dimers, $\text{Pt}_2(\text{SO}_4)_4^{2-}$ and $\text{Pt}_2(\text{HPO}_4)_4^{2-}$, by means of reverse disproportionation. For the source of platinum(IV) we will use the polymer that forms in strong acid; the platinum(II) will be supplied by $\text{Pt}(\text{H}_2\text{O})_4^{2+}$ dissolved in strong acid.

Reactions with Sulfuric Acid

A solution of $\text{Pt}(\text{H}_2\text{O})_4^{2+}$ in sulfuric acid was prepared by precipitating the neutral solid from 75 ml of a 0.01M stock solution of the complex in 1M perchloric acid with 1M sodium hydroxide, and dissolving this solid in approximately 1 mL of concentrated sulfuric acid; the resulting solution became quite hot. An external D_2O insert was added for lock, and an NMR spectrum as shown in Figure 40 was obtained. Note the downfield shift of all peaks by as much as 554 ppm (Table 16) due to the high acidity of the solution. One new resonance was observed at 629ppm; this resonance is assigned to $\text{Pt}(\text{SO}_4)_3(\text{H}_2\text{O})_1$, based upon the consistent, sequential shift of the platinum resonances of the compounds as progressive substitution occurs.

A solution of platinum(IV) was prepared by dissolving 135.4 mg of $\text{Na}_2\text{Pt}(\text{OH})_6$ in approximately 1 mL of concentrated sulfuric acid; a D_2O insert was added, but as expected no platinum resonances were observed (the sample was 2-3 hours old.)

The two solutions were mixed together, and a new resonance was observed (Figure 42) at 1878 ppm (linewidth approximately 700 hz.) This resonance compares exactly with that observed for $\text{Pt}_2(\text{SO}_4)_4^{2-}$ prepared by literature methods and dissolved in concentrated sulfuric acid (Figure 43), the resonance of which falls at 1896 pm

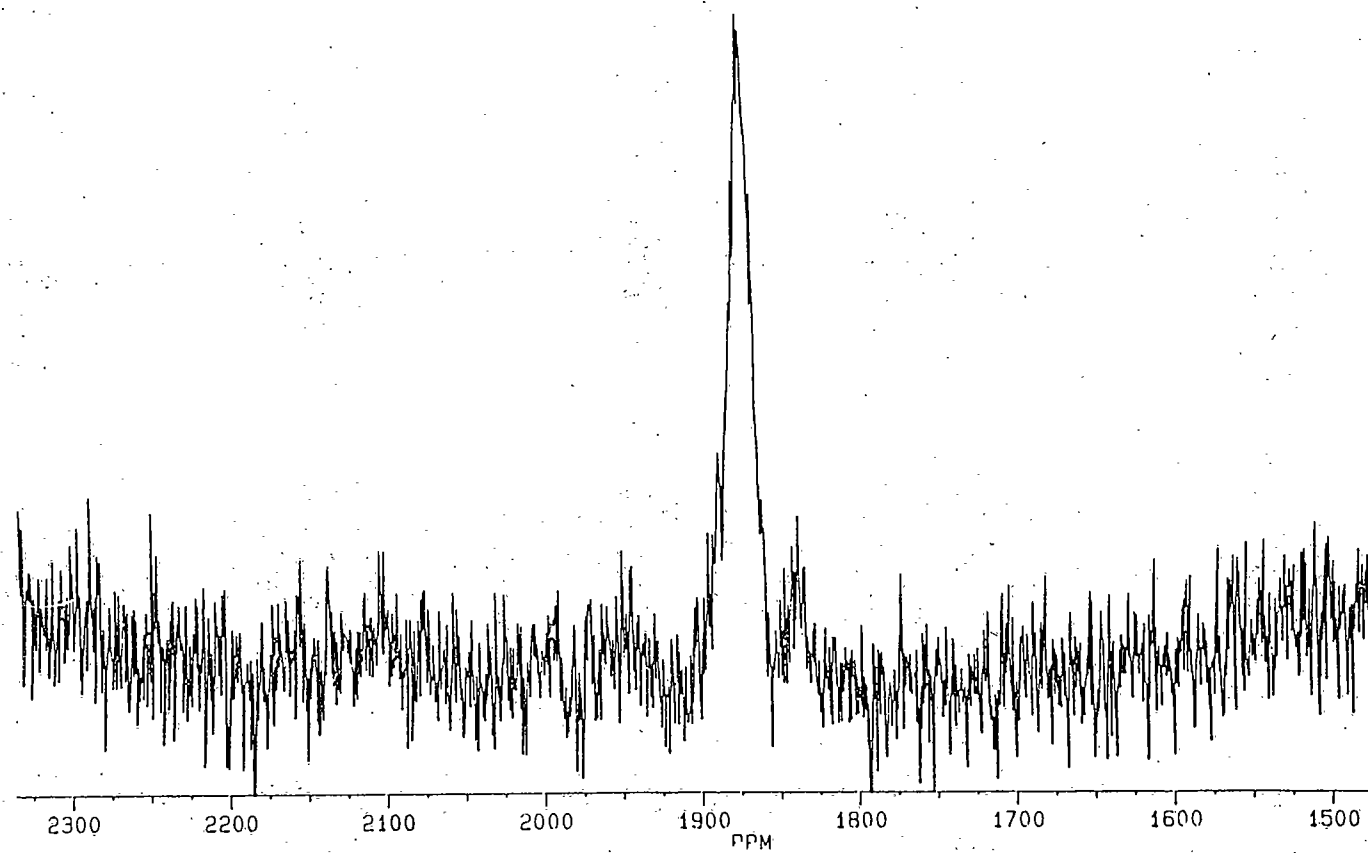


Figure 42. ^{195}Pt NMR Spectrum of Reverse Disproportionation Synthesis of $\text{Pt}_2(\text{SO}_4)_2^{2-}$ in Concentrated H_2SO_4 .

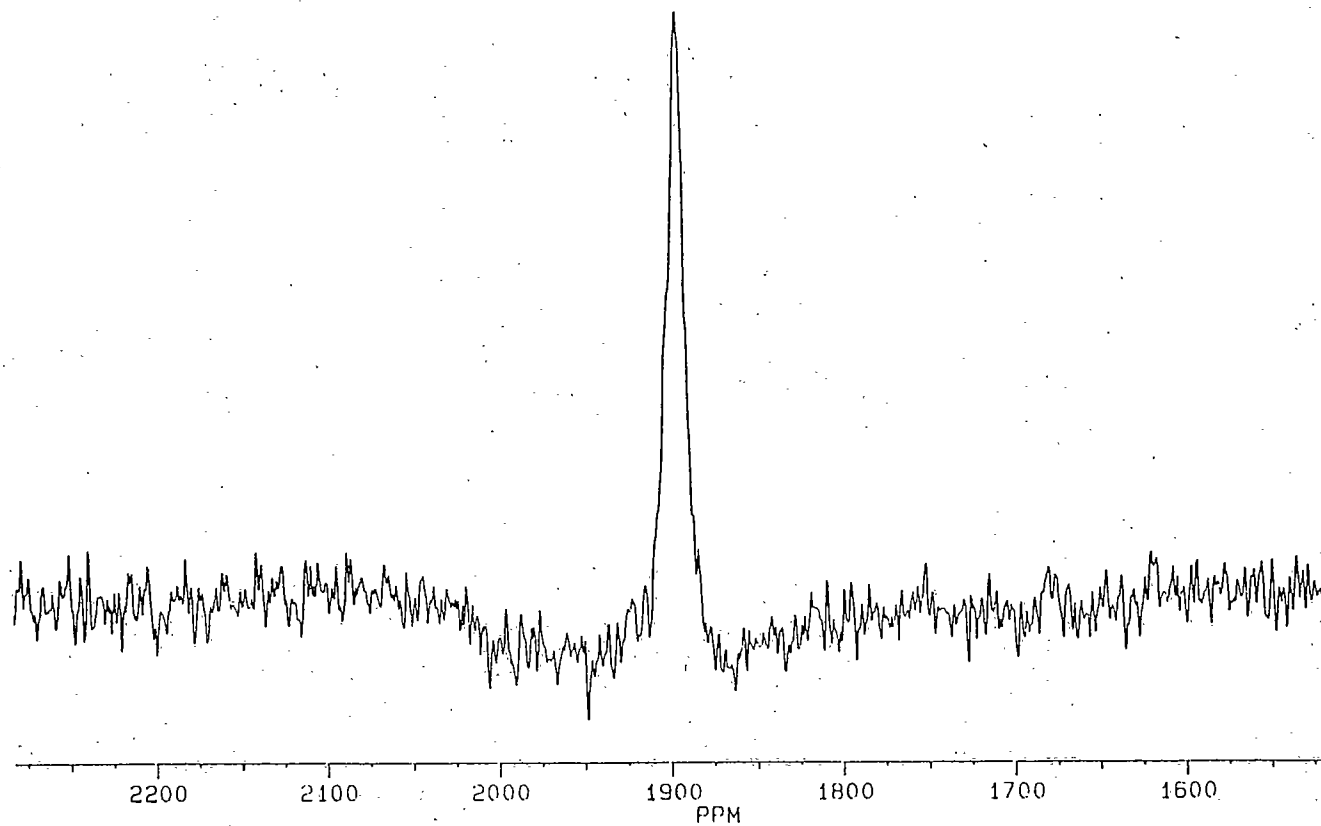


Figure 43. ^{195}Pt NMR Spectrum of Literature Preparation of $\text{Pt}_2(\text{SO}_4)_4^{2-}$ in Concentrated H_2SO_4 .

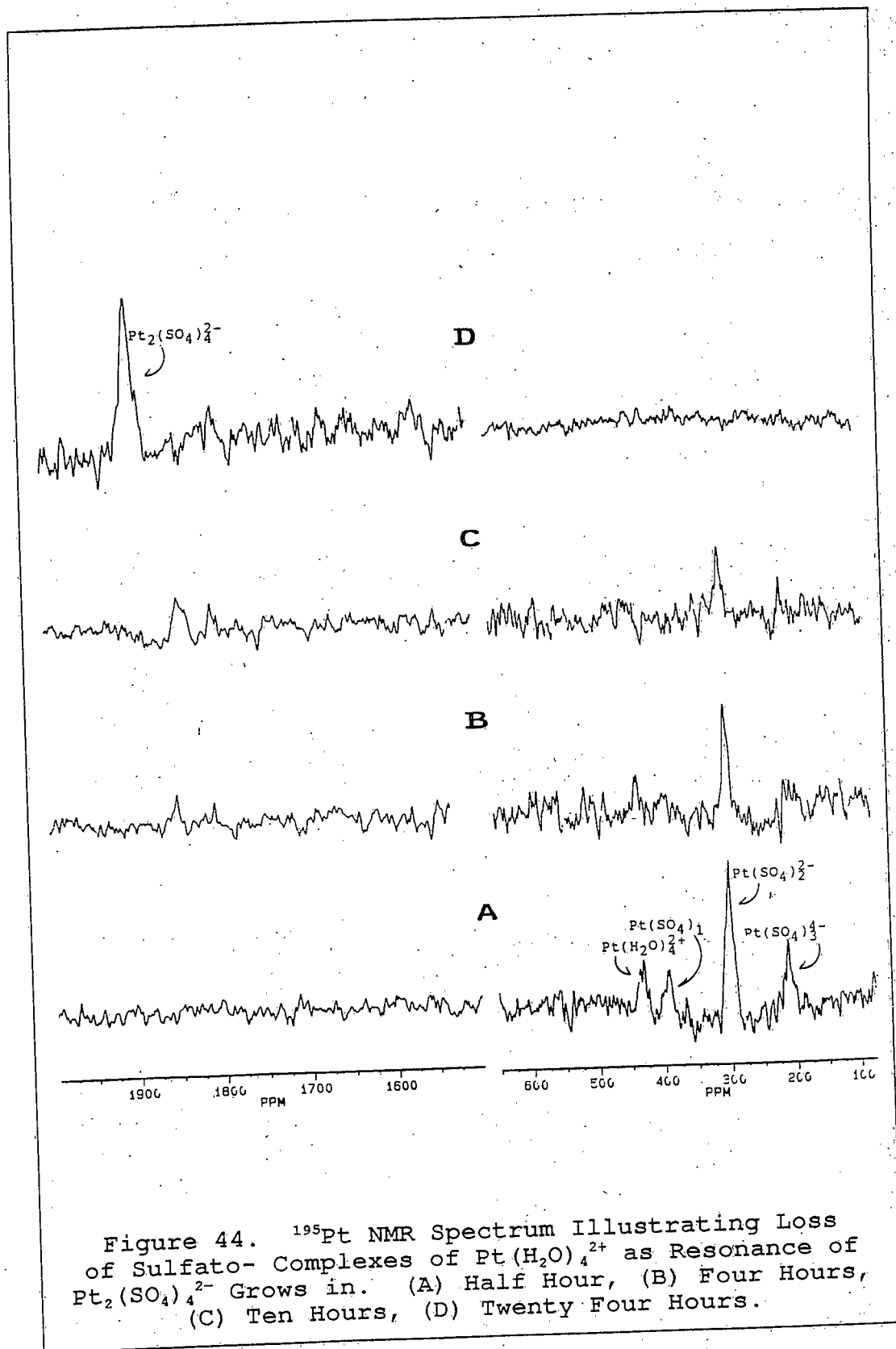
(linewidth= 573 hz).

As further demonstration that the dimer peak arose from the reaction of platinum(II) and platinum(IV), Figure 44 shows the gradual loss over time (3 hour increments) of the platinum(II) peaks, and growth of the $\text{Pt}_2(\text{SO}_4)_4^{2-}$ resonance. There appeared to be no preferential loss of one platinum(II) species over another -- all peaks lost intensity at the same rate. The identity of the platinum(III) resonance was further confirmed by addition of the literature preparation of the dimer to this sample, yielding only one peak with larger area.

Reactions in Phosphoric Acid

Formation of the platinum(III) phosphate dimer, $\text{Pt}_2(\text{HPO}_4)_4^{2-}$, was attempted in the same manner. The neutral solid precipitated from 35 mL of the 0.01M $\text{Pt}(\text{H}_2\text{O})_4^{2+}$ stock solution with 1M NaOH was dissolved in 50% phosphoric acid/ H_2O to give the spectrum in Figure 41. The resonances of the multiply substituted complexes are shifted downfield somewhat from the reported resonances (Table 17). The hydrogenphosphate substituted species seemed to shift downfield less than for the sulfate species.

To this solution was added 40 mg of $\text{Pt}(\text{OH})_6^{2-}$, and the resulting solution was heated at 70°C for 15 minutes.



Long NMR accumulation (177,000 scans) showed a peak at 1897 ppm (linewidth= 250hz, Figure 45). This resonance is assigned to the $\text{Pt}_2(\text{HPO}_4)_4^{2-}$ complex; the resonance for the compound prepared by literature methods and dissolved in 50% phosphoric acid falls at 1892 ppm. Addition of the known compound to solutions of the reverse disproportionation preparation showed only one peak at the same chemical shift as for the new synthesis, with increased area.

The ^{31}P NMR spectrum of the new preparation (Figure 46), showed resonances at 7.6 and 21.2 ppm; these peaks agreed well with the resonances reported at 8.6 ppm for the singly substituted platinum(II) complex $(\text{Pt}(\text{HPO}_4)(\text{H}_2\text{O})_3)$, and at 21.3 ppm for the platinum(III) phosphate dimer $(\text{Pt}_2(\text{HPO}_4)_4^{2-})$. The linewidths of the resonances are 50 and 27 Hz, respectively; the linewidth of the dimeric compound is sufficiently large under reaction conditions (50% H_3PO_4) so as to prevent the resolution of the 36 Hz $^2J_{\text{P-O-Pt}}$ coupling reported (at the height at which the platinum resonances would be observed, the peak is 40 Hz wide.) The resonances of the other monomeric platinum(II) complexes were obscured beneath the intense phosphate resonance at zero ppm.

Synopsis of Reverse Disproportionation and Platinum(IV) Polymerization Results

We have formed several new mononuclear platinum(II)

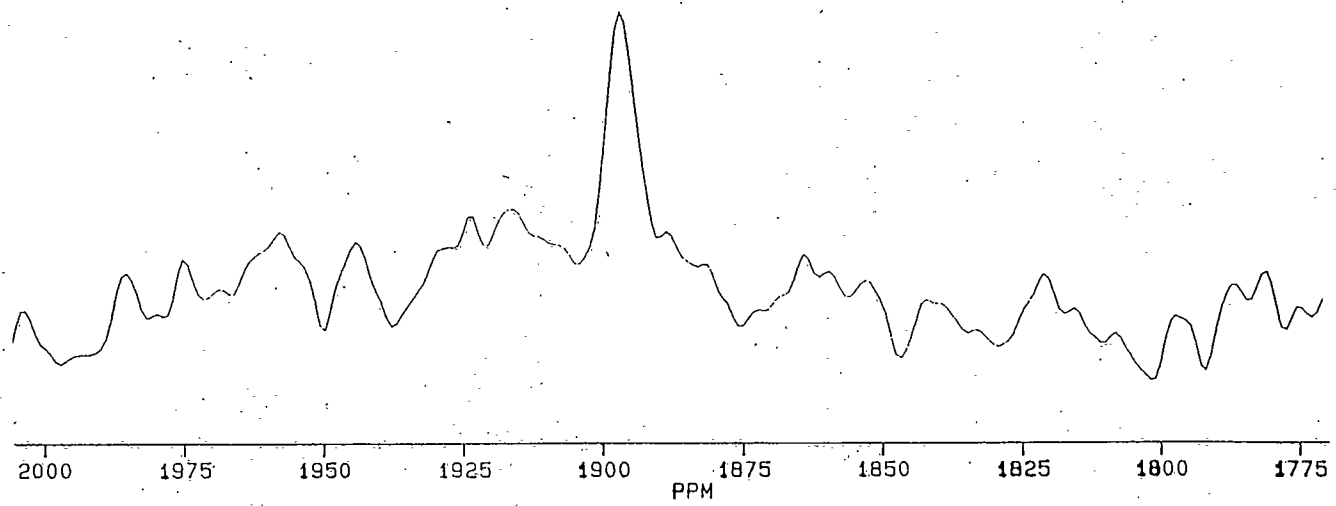


Figure 45. ^{195}Pt NMR Spectrum of Reverse Disproportionation Synthesis of $\text{Pt}_2(\text{HPO}_4)_4^{2-}$ in 50% H_3PO_4 .

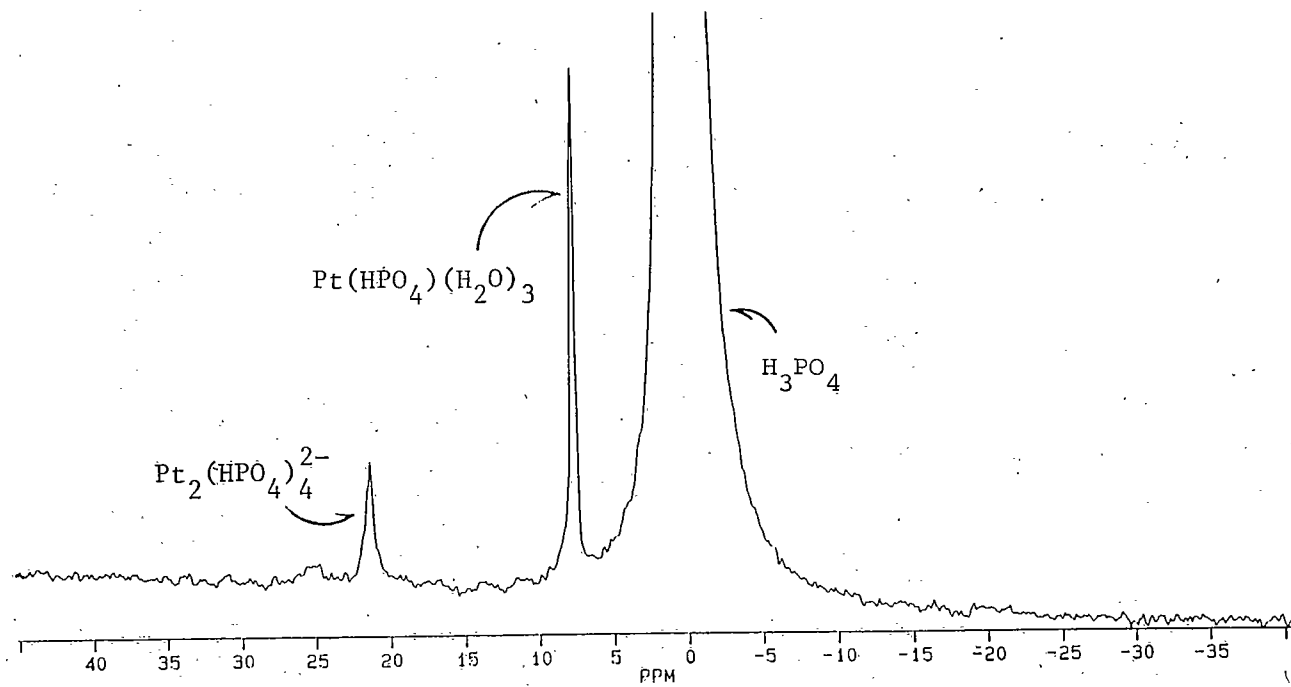


Figure 46. ^{31}P NMR Spectrum of Reverse Disproportionation Synthesis of $\text{Pt}_2(\text{HPO}_4)_4^{2-}$ in 50% H_3PO_4 .

and platinum(IV) complexes and identified them using ^{195}Pt NMR spectroscopy, we have demonstrated the polymerization of platinum(IV) in acid solution (and platinum(II) under some conditions), and the viability of reverse disproportionation to form platinum clusters has also been demonstrated.

While the formation of platinum (III) dimers can proceed through reverse disproportionation, the utility of this method for synthesizing isolable quantities of compound is probably poor. The ^{195}Pt NMR resonances reported for the reverse disproportionation formation of the sulfate and phosphate dimers indicated the species were present in low concentration; by far the large majority of platinum in solution is unobserved as polymer. The literature syntheses for the compounds isolate solid when it precipitates from solution; no precipitation was ever observed in the reverse disproportionation reactions (probably due to low concentrations), and thus isolation of the desired complexes from solution would be difficult.

It may be possible, however, to use the method of reverse disproportionation to form new multinuclear platinum complexes, and identify these compounds using NMR spectroscopy. In what types of conditions might we expect new complexes to form? The two known platinum(III) dimers formed in the concentrated acid of

the coordinated ligand; perhaps we can perform these same kind of reactions in different acids, and watch for new platinum resonances in the region in which the resonances for $\text{Pt}_2(\text{SO}_4)_4^{2-}$ and $\text{Pt}_2(\text{HPO}_4)_4^{2-}$ are observed (around 1700-2000ppm).

Since we know that platinum(IV) polymerizes in strongly acidic solutions, and we still wish to observe the platinum(IV) resonances decrease as the compounds react with platinum(II) to form the dimer, it seems reasonable to use less acidic acids in which to run the reaction. If we use strong organic acids, like trifluoroacetic or trichloroacetic acids, perhaps the polymerization will be decreased enough by the lower acidity (compared to sulfuric and phosphoric acids) to permit the observation of platinum(IV) complexes. We also must study the reaction behavior of platinum(II) in these acids, so we understand the system thoroughly.

Well Characterized Reactions of Platinum(II) and Platinum(IV) with Organic Acids

Reactions of Platinum(II) and Platinum(IV) with Trifluoroacetic Acid

Platinum (II)

Trifluoroacetic Acid solutions of $\text{Pt}(\text{H}_2\text{O})_4^{2+}$ in perchloric acid showed sequential substitution for water (see Figure 47) as the TFA concentration went from 1 M to 5 M, at which point all $\text{Pt}(\text{H}_2\text{O})_4^{2+}$ was gone. When the

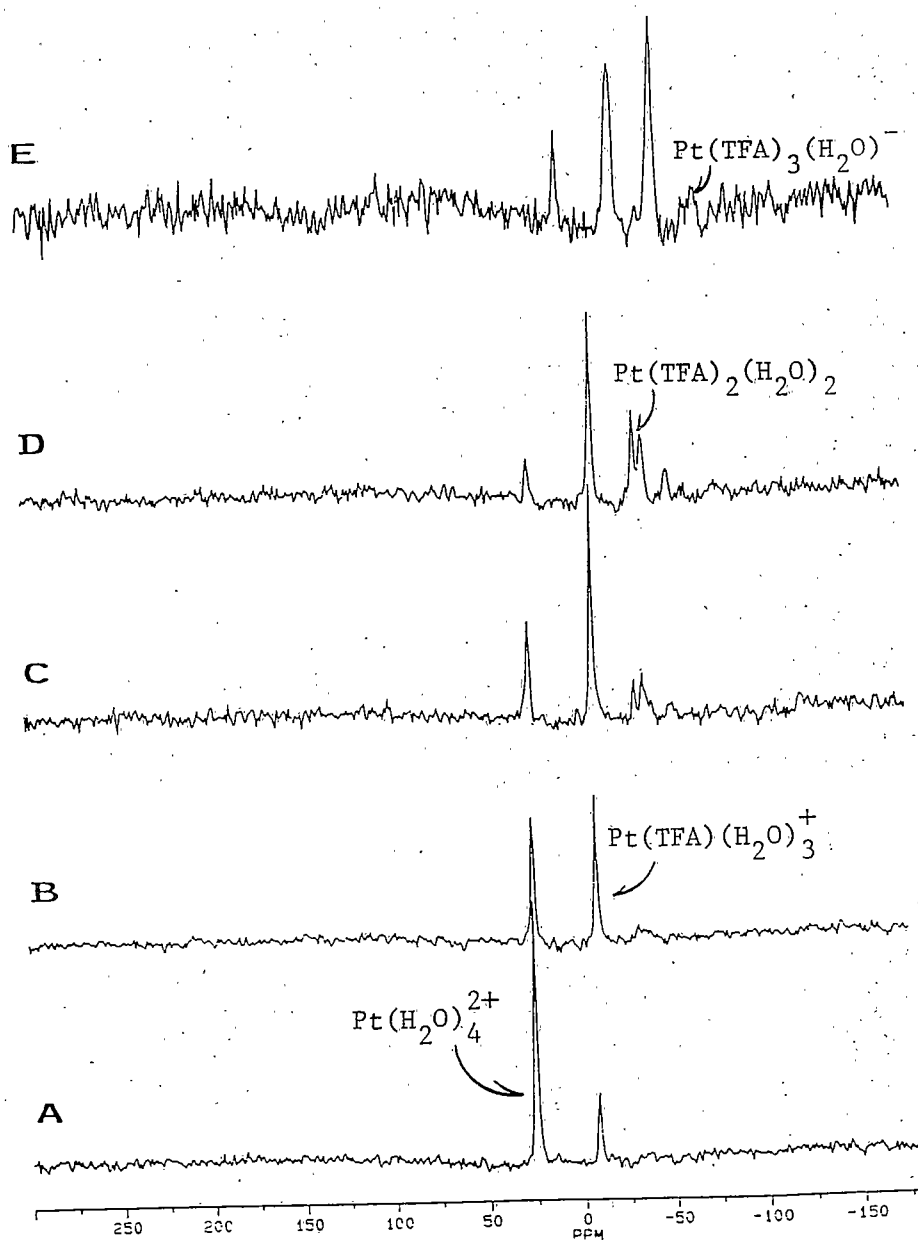
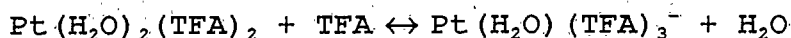
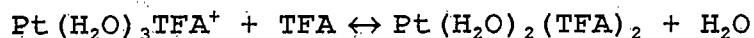
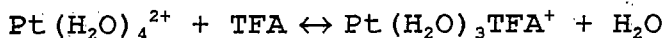


Figure 47. ^{195}Pt NMR Spectrum of TFA Complexes of $\text{Pt}(\text{H}_2\text{O})_4^{2+}$ in 1M HClO_4 . (A) 20 Min. (1M TFA), (B) 90 Min., (C) 2 1/2 Hrs., (D) 17 Hrs., (E) 19 Hrs. (5M TFA)

concentration of TFA was 1 M, in the bottom four spectra (A-D), even with heating at 70° substitution was slow--heating for 10 minutes at 70° showed no change in the platinum spectrum (A); as time progressed the mono-TFA species began to predominate in intensity over the tetraaqua species, and the two bis-TFA species began to form (B-D). After approximately 31 hours substitution of water was only seen up to the formation of the tris-species, and no further (D). Increase of the TFA concentration to 2 M, 3 M, or 4 M showed no noticeable change in the spectrum, even with heating, except for a progressive downfield shift. At 5 M TFA (E), the resonances had shifted 10 to 15 ppm downfield, and broadened such that the two bis-species coalesced into a single resonance at -44ppm.

Equilibrium having been established between the four initially substituted species, the equilibrium constants for the formation of the species:



were determined from the integrals of the NMR spectrum to be 3.00 L/M, 1.05 L/M, 1.05 L/M, and 0.42 L/M for the mono-, cis- and trans- bis-, and tris- TFA species, respectively. Not knowing the relative trans- directing

strength of TFA compared to water prevented the cis- or trans- assignment of the two bis- isomers. Note the downfield shift of the peaks as the acidity of the solution increased, due to the increase in TFA concentration from one molar to five molar; this was probably due to rapid proton exchange on the ligand as the proton concentration increased.

Solutions of $\text{Pt}(\text{H}_2\text{O})_4^{2+}$ in 1 M TFA in D_2O (Figure 48A) rapidly reached equilibrium (within 15 minutes at room temperature) to form the mono-, and cis- and trans- bis-complexes (see Table 18.) The resonances of these species broadened and the solution turned blue within one hour; within one hour and thirty-five minutes the peaks were gone (Figure 48B.) This is the same effect reported by Appleton/Hall(106) for reactions of the tetraaquaplatinum(II) ion with acetic acid in the presence of air (the molecules form stacked oligomers.) The peaks were shifted downfield compared to the resonances in 1 M perchloric acid.

Table 18. ^{195}Pt NMR Resonances of Platinum(II) TFA Complexes.				
acid strength	$\text{Pt}(\text{H}_2\text{O})_4^{2+}$	$\text{Pt}(\text{TFA})^+$	$\text{Pt}(\text{TFA})_2$	$\text{Pt}(\text{TFA})_3^-$
1-4M TFA	24ppm	-10ppm	-33ppm -37	-44ppm
5M TFA	8	-25	-44	-68

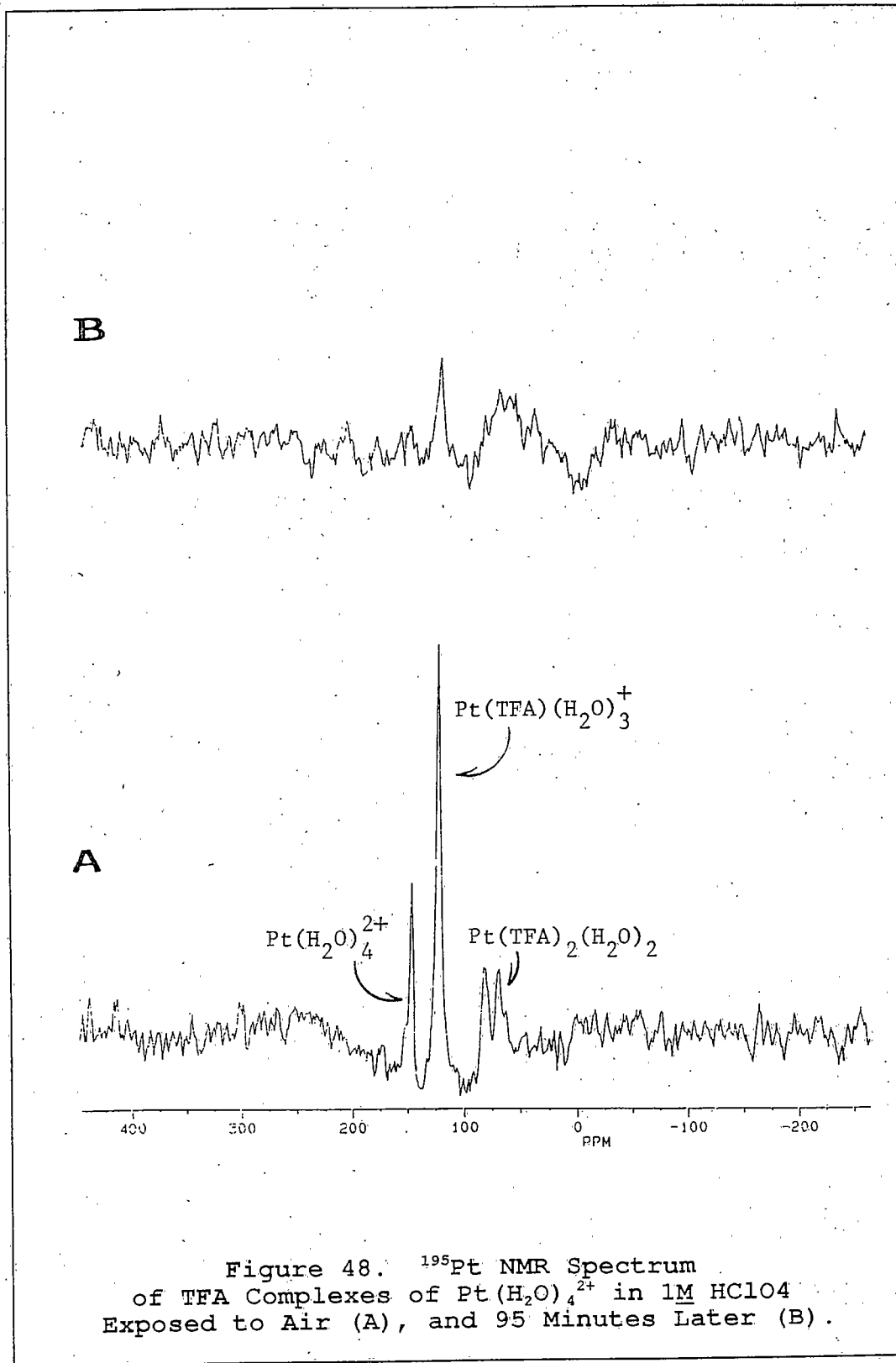


Figure 48. ^{195}Pt NMR Spectrum of TFA Complexes of $\text{Pt}(\text{H}_2\text{O})_4^{2+}$ in 1M HClO_4 Exposed to Air (A), and 95 Minutes Later (B).

Potassium tetranitritoplatinate(II), $K_2Pt(NO_2)_4$, reacted in neat TFA after refluxing 20 minutes to liberate brown gas and form a clear red solution; no further change was observed after 2 hours. The ^{195}Pt NMR spectrum of this solution (Figure 49) showed resonances of two different species: -189.5 and -945.0 ppm. These resonances could be due to simple partial substitution of the nitrite ion by TFA, to form compounds like $(NO_2)_{4-x}(CF_3CO_2)_xPt^{x-6}$; these compounds would be shifted downfield from the $Pt(NO_2)_2^{2-}$ ion resonance at -2168 ppm.

Platinum(IV)

The reaction of platinum(IV), either in the form of neutral platonic acid, or as $Na_2Pt(OH)_6$, with TFA formed several highly substituted compounds; as more ligand coordinated to the metal atom, sequential downfield shifts of about 100 ppm were observed, as well as downfield shifts of all resonances as the relative concentration of TFA was increased (Figure 50.) Figure 51 shows the ^{195}Pt NMR spectra of the species formed when platonic acid was reacted with 50% TFA in D_2O . Initially a simple distribution of $Pt(OH)_6^{2-}$ and the mono- and cis- and trans- bis- complexes was formed (A); as time progressed the more highly substituted compounds predominated, yielding an equilibrium mixture of the mono-, bis-, and tris- species. No higher substitutions were observed in 50% TFA, even with heating at 70°C.

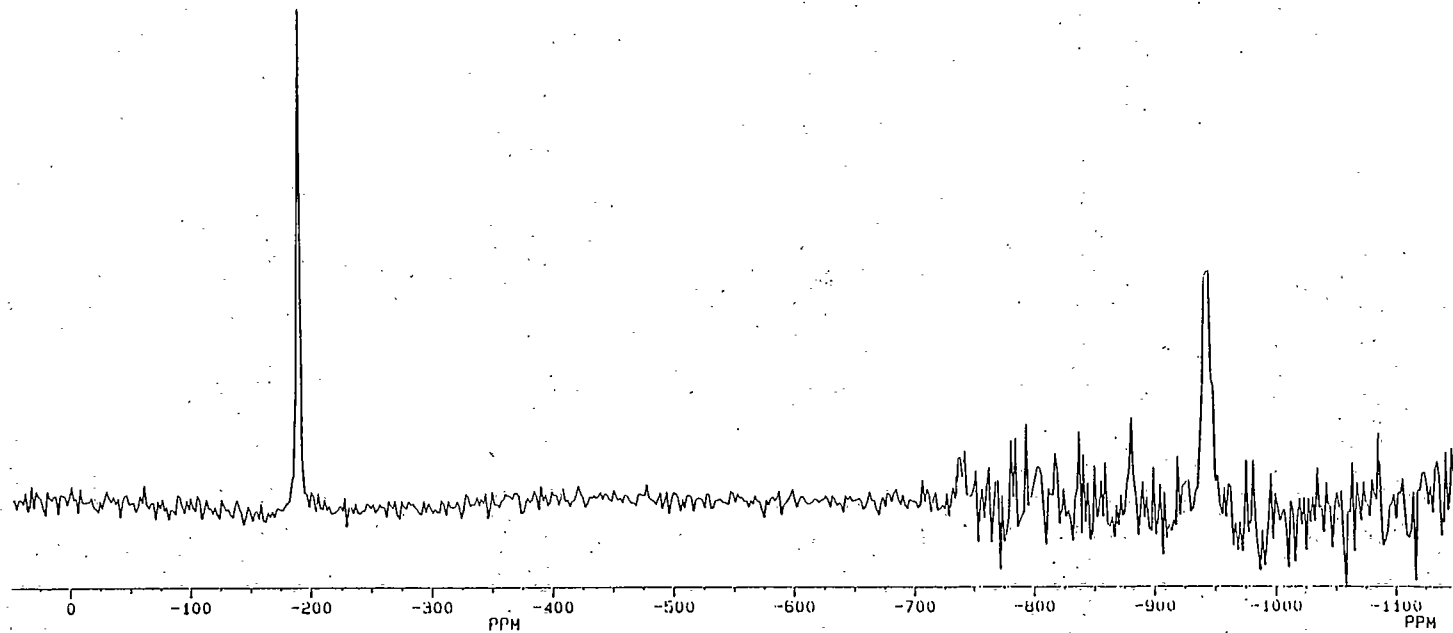
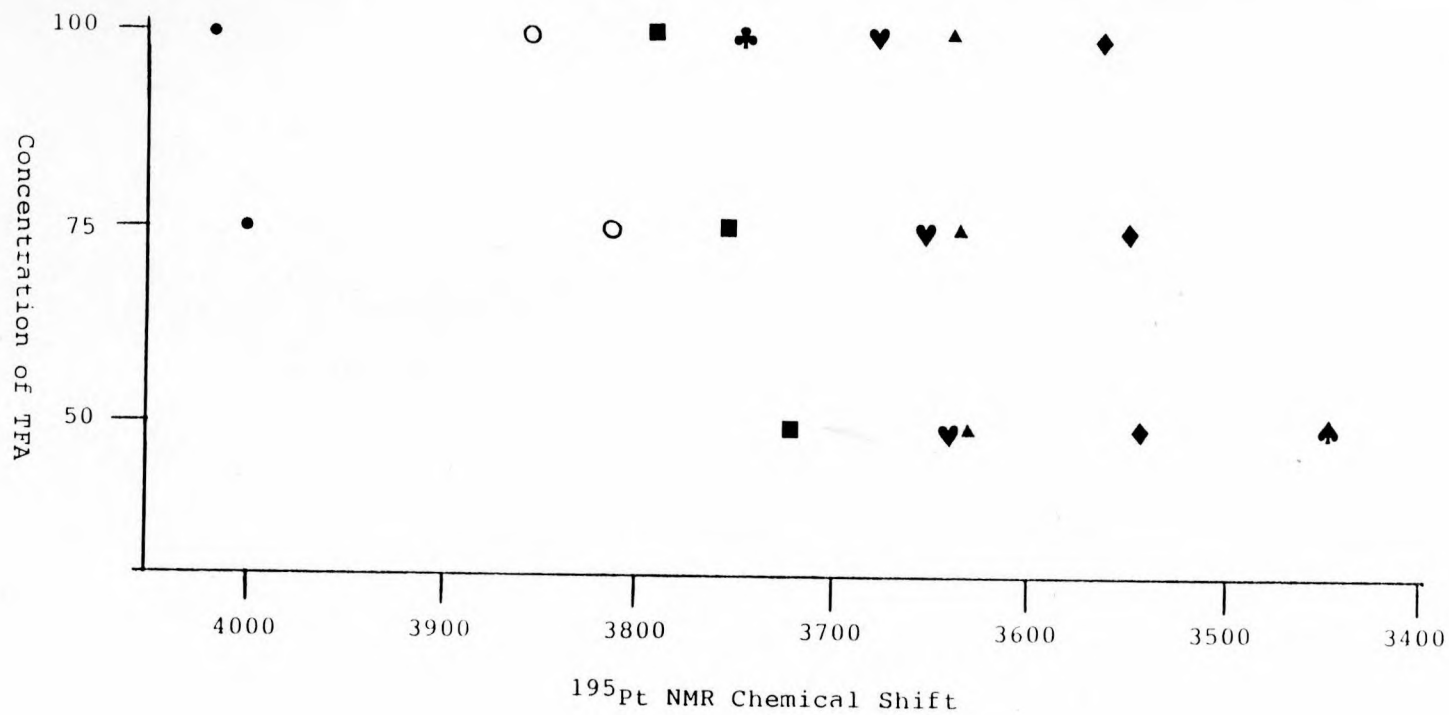
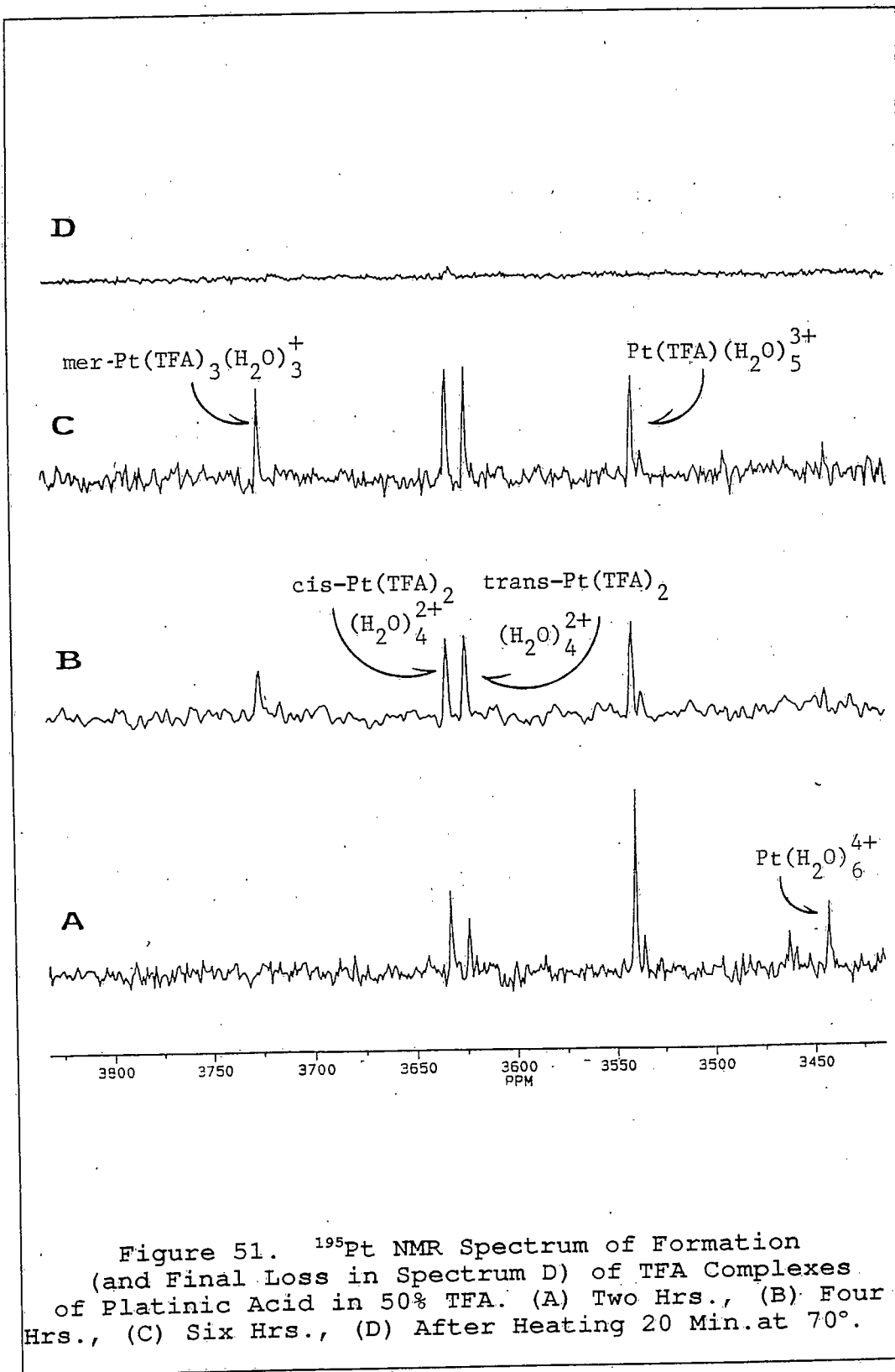


Figure 49. ^{195}Pt NMR Spectrum of $\text{Pt}(\text{NO}_2)_4^{2-}$ in Concentrated TFA.



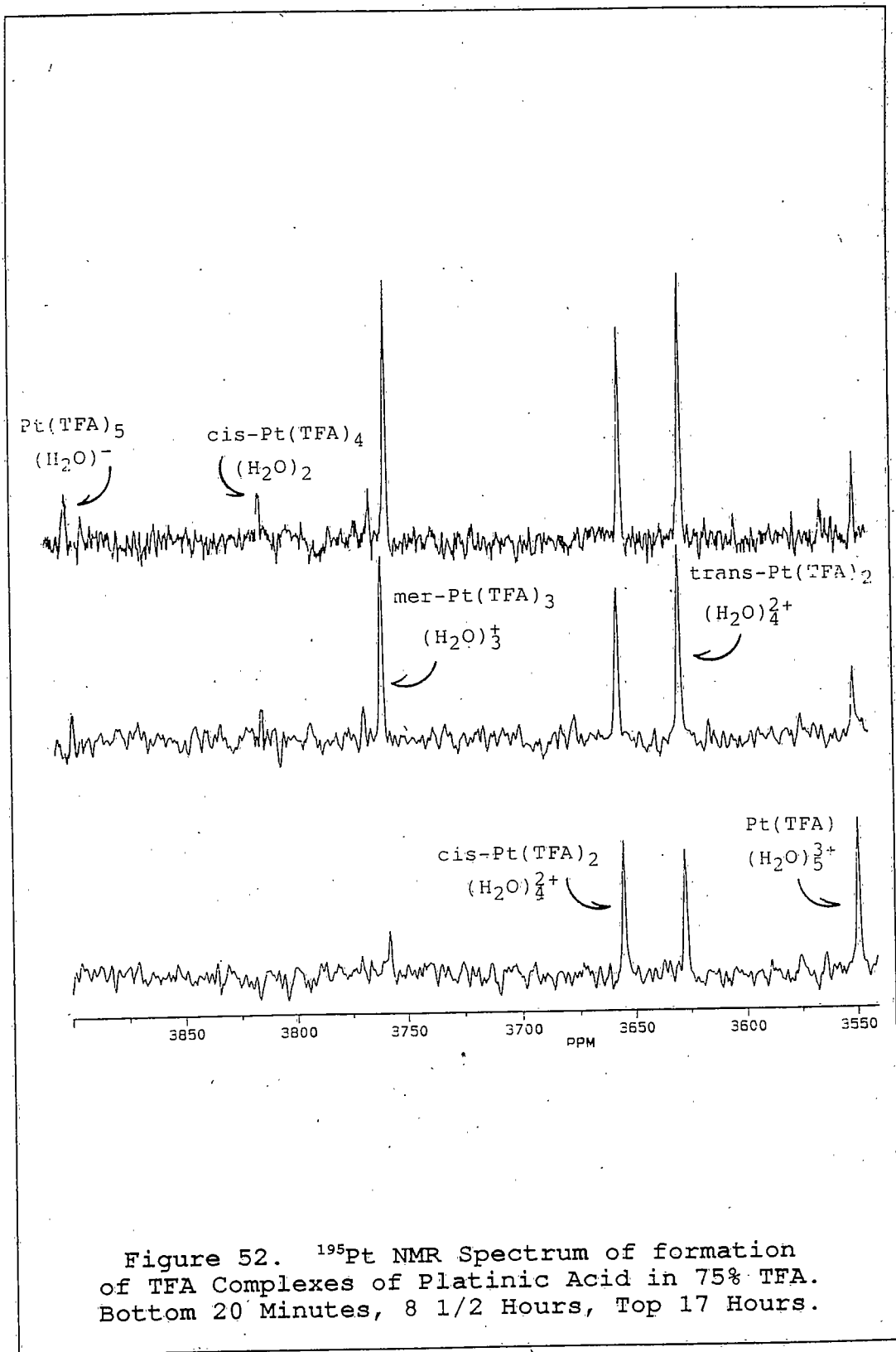
• Pt(TFA)₅H₂O⁻ ○ cis-Pt(TFA)₄(H₂O)₂ ■ mer-Pt(TFA)₃(H₂O)₃⁺
 ♣ fac-Pt(TFA)₃(H₂O)₃⁺ ♥ cis-Pt(TFA)₂(H₂O)₄²⁺ ▲ trans-Pt(TFA)₂(H₂O)₄²⁺
 ◆ Pt(TFA)(H₂O)₅³⁺ ♠ Pt(H₂O)₆⁴⁺

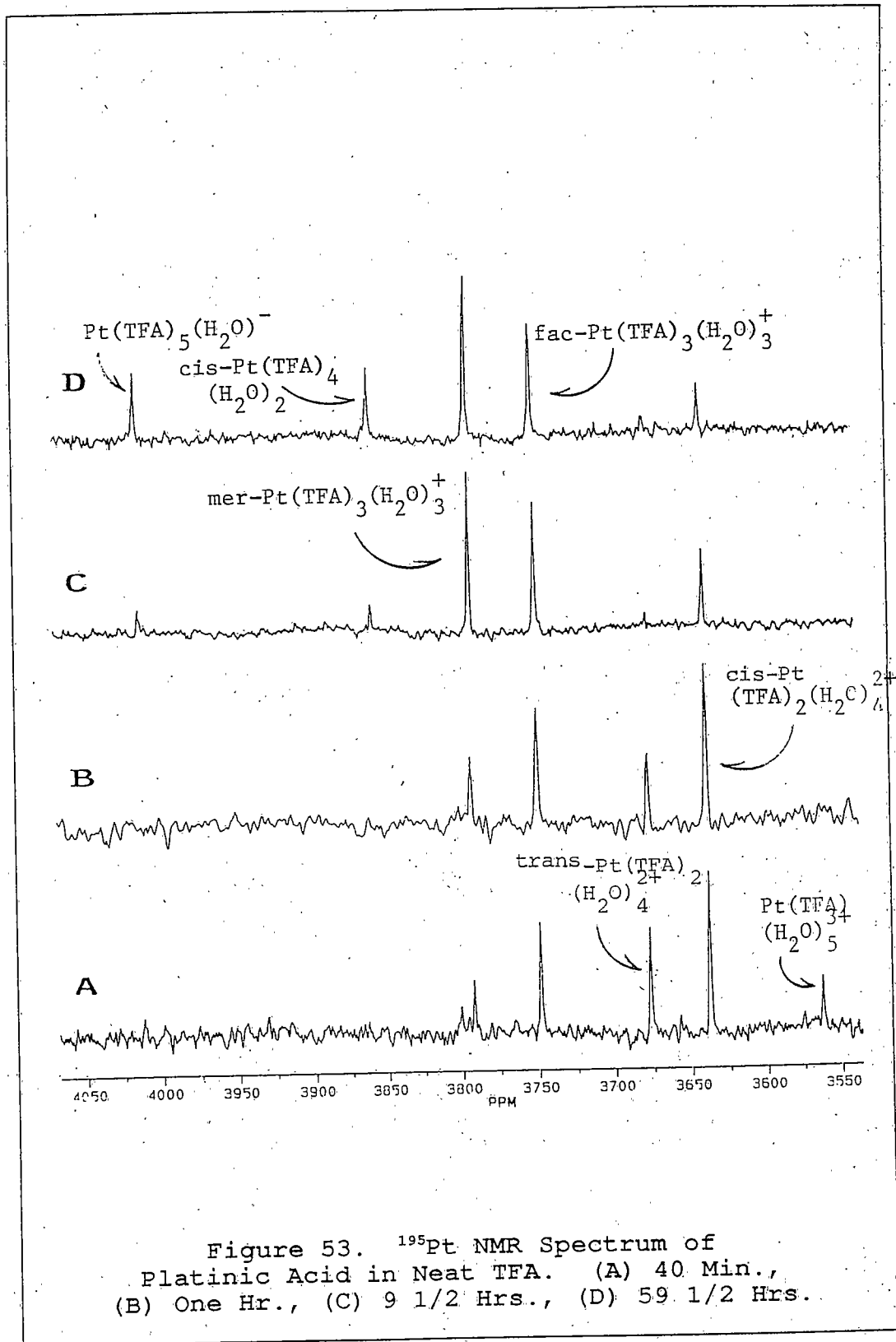
Figure 50. Diagram Illustrating Chemical Shift of ¹⁹⁵Pt NMR Resonances of TFA complexes of Platinic Acid in 50%, 75%, and 100% TFA.



For solutions of platinic acid in 75% TFA similar distributions of species were observed, as well as further substitution to tetrakis- (3815 ppm) and pentakis- (4001 ppm) species (Figure 52); the relative intensities of the resonances for these more highly substituted compounds allowed us to assign the tris-compound to its geometrical isomer. As only one tris-species (3757.5 ppm, A-C) is formed from an essentially equal mixture of the bis-species, this resonance must be due to the meridional isomer, as it is the only isomer that can arise from both the cis- and trans-disubstituted isomers. Also note that even the initial spectra showed no $\text{Pt}(\text{OH})_6^{2-}$; at 75% TFA the ligand concentration was too high and had driven the relative concentration of the unsubstituted species down to the point at which it was unobservable under the experimental conditions.

Platinic acid in neat TFA (Figure 53) showed one new resonance over the reactions in 75% TFA; this resonance fell at 3749 ppm, and corresponds to the facial tris-species unobserved in the less concentrated reactions (A,B.) Since the relative intensities of the tris-, tetrakis-, and pentakis-species all increased together over time in neat TFA, the tetrakis species must arise from both the meridional and facial tris-isomers; this dictates that the tetrakis resonance at 3860 must correspond to the cis-isomer, the only isomer that can





arise from both meridional and facial isomers.

The bis- isomers can now be assigned due the change in intensities of the bis- resonances as the tris-species grow. The bis- resonance that lay further downfield at 3676.5 ppm lost intensity more rapidly than the upfield peak at 3637.3 ppm as the new facial tris-isomer grew larger; this suggests that the downfield bis-peak must be cis- (the only isomer from which a facial geometry can arise), leaving the upfield peak as trans-.

Mixtures of Platinum (II) and Platinum (IV)

Reactions in 50% Trifluoroacetic Acid When Platinic acid and tetraaquaplatinate were mixed in 50% TFA the ^{195}Pt NMR spectra of the platinum(II) and platinum(IV) regions appeared the same as the unmixed reactions; when heated at 70°C for 15 minutes, however, the platinum(IV) peaks drastically lost intensity and disappeared (Figure 51D), while the platinum(II) spectrum remained essentially unchanged.

In addition to the spectral changes noted above, a new peak was observed at 2421 ppm (Figure 54.) The chemical shift of this resonance is between the platinum(II) and platinum(IV) species, just as the resonances of the platinum(III) dimers of sulfate and phosphate were observed. While the resonances of the two known compounds fall more nearly half-way between the platinum(II)

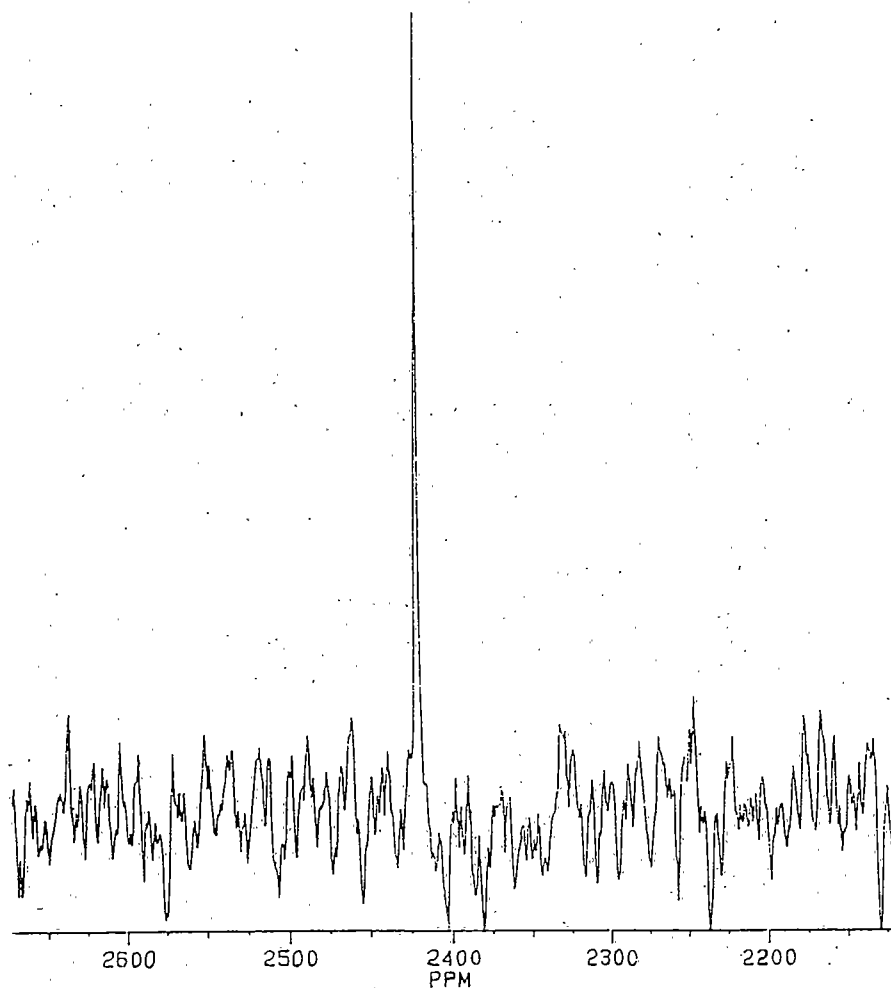


Figure 54. ^{195}Pt NMR Spectrum of New Peak Observed upon Addition of $\text{Pt}(\text{H}_2\text{O})_4^{2+}$ to Equilibrated TFA Complexes of Platinic Acid in 50% TFA.

and platinum(IV) regions, it is not unreasonable to suggest that this new resonance corresponds to a platinum(III) TFA dimer; the shift of the resonance of about 650 ppm relative to the chemical shifts of the known dimers could be due to more interaction between the ligand and free protons than is observed for sulfate and phosphate; as the TFA ligand is a better base than sulfate or phosphate (weaker acid, stronger conjugate base), the higher basicity of the TFA ligand would introduce more interactions with free protons in solution, and allow for a large downfield shift with respect to the resonances for the known platinum(III) dimers.

Reactions in neat trifluoroacetic acid Upon addition of tetraaquaplatinum(II) ion to a solution of platinic acid in neat TFA, an immediate change was observed in the platinum(IV) spectrum (Figure 55.) All resonances broadened, and the resonances corresponding to the tetrakis-, tris-, and cis-bis- species disappeared; the only resonances remaining were those of the pentakis- and trans-bis- species, while the cis- peak grew in at 3678 ppm, as well as a new broad peak falling at 3765.9 ppm, between the positions of the two tris-isomers.

The platinum(II) spectrum changed as well (Figure 56); the most reactive platinum(II) species appeared to be those of intermediate substitution, because these

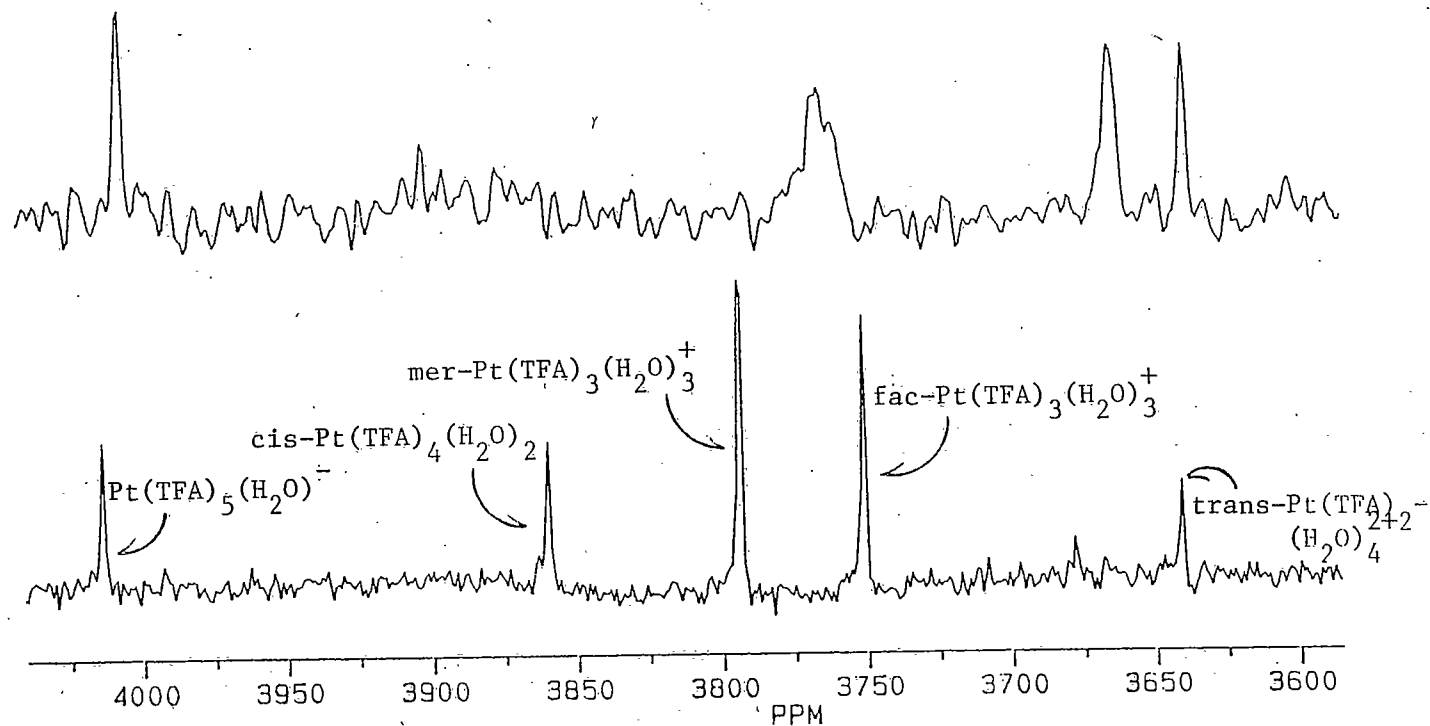


Figure 55. ^{195}Pt NMR Spectrum of TFA
 Complexes of Platinic Acid in Concentrated TFA
 Before (bottom) and 135 Minutes After Addition of $\text{Pt(H}_2\text{O)}_4^{2+}$ (top).

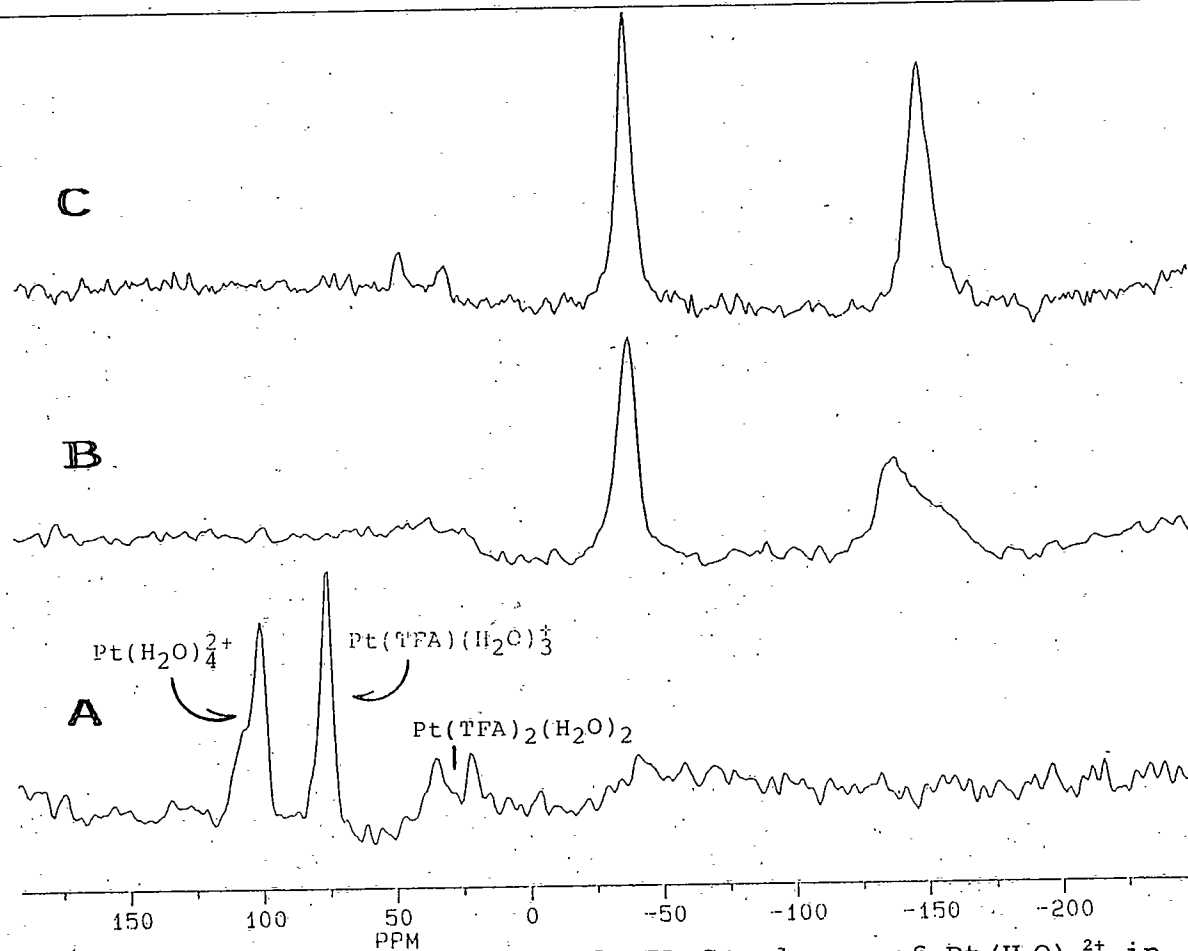


Figure 56. ^{195}Pt NMR Spectrum of TFA Complexes of $\text{Pt}(\text{H}_2\text{O})_4^{2+}$ in Concentrated TFA Before and After Addition of Platinic Acid in Concentrated TFA. (A) Initial Solution, (B) 185 Minutes After Addition, (C) 24 Hours

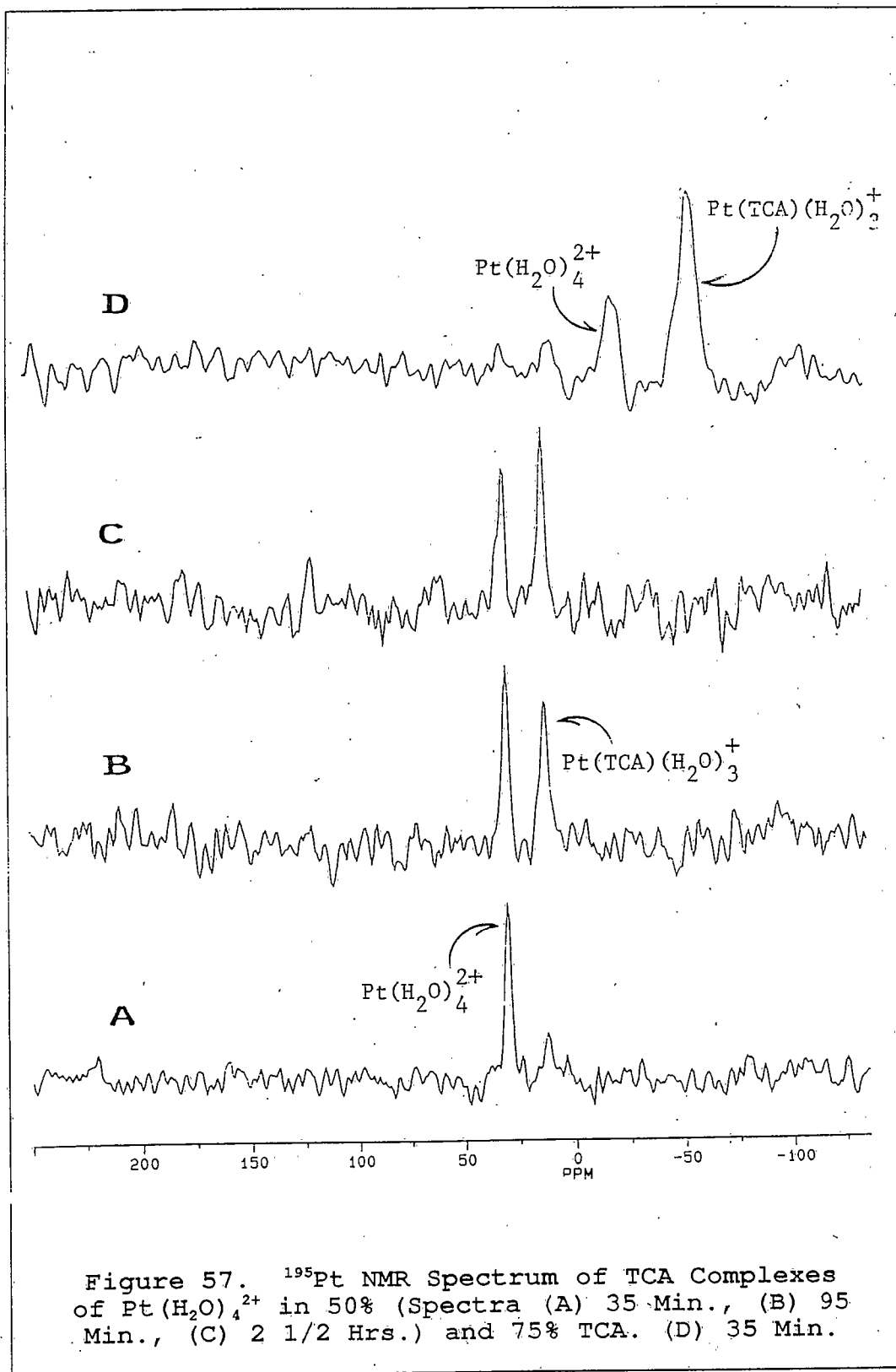
resonances disappeared; the resonances of the two more highly substituted platinum(II) species, however, did not change. Two new resonances grew in further upfield at -38.5 and -148.5 ppm; these new resonances were very broad (350hz) and indicated further substitutions on the platinum atom, undoubtedly involving the platinum(IV). These platinum(II) resonances persisted for days.

Platinum(IV) dissolved in base before addition of trifluoroacetic acid Solutions of hexahydroxoplatinate in 1 M NaOH acidified with neat TFA to attain a solution 50% in TFA showed the same equilibrium distributions as for solutions made from direct solution of platinic acid or hexahydroxoplatinate in 50% TFA solution, with the exception that all resonances were shifted dowfield 15-23 ppm.

Reactions of Platinum(II) and Platinum(IV)
with Trichloroacetic Acid

Platinum(II)

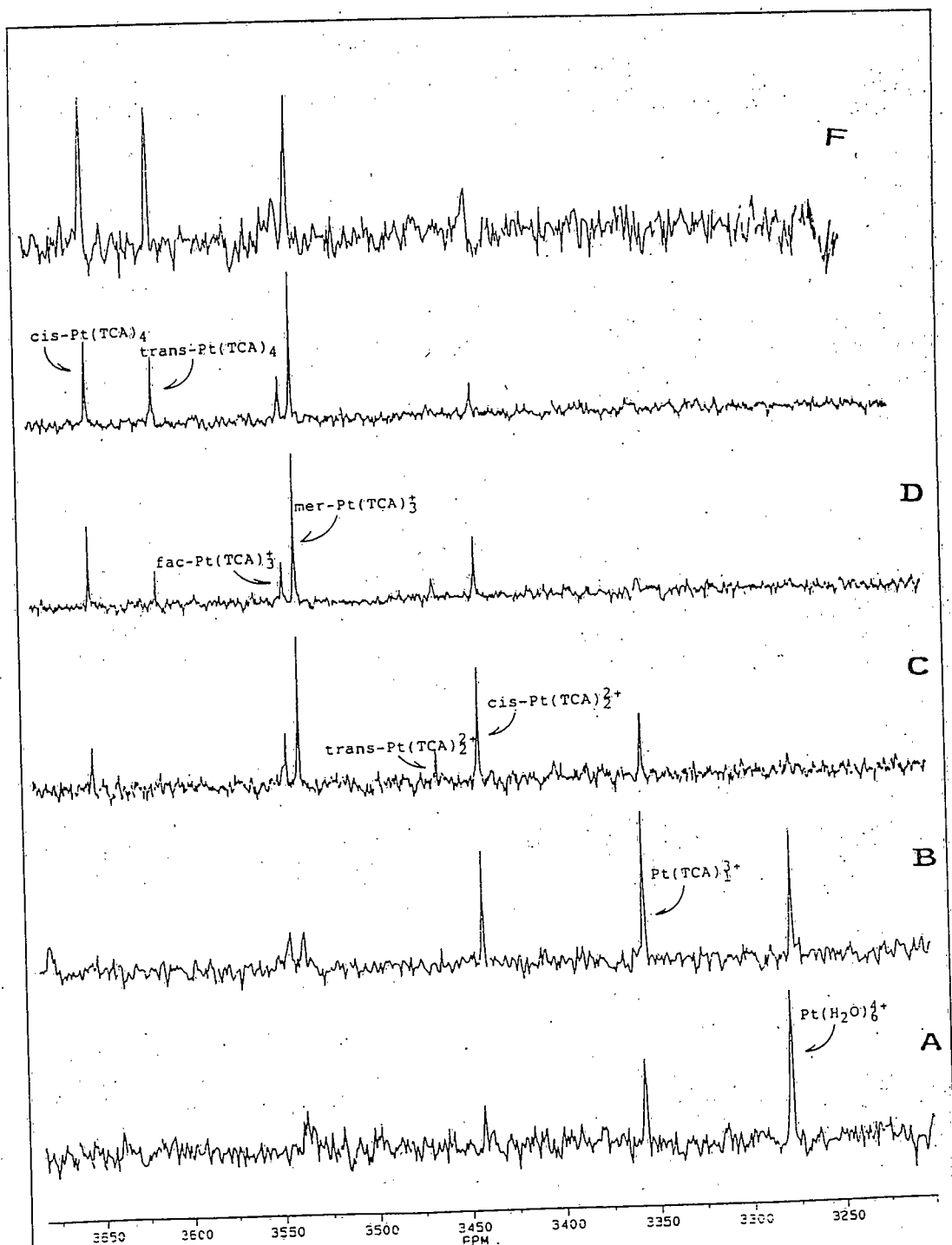
Reaction of the tetraaquaplatinum(II) ion with a solution of 50% TCA in D₂O yielded a compound containing only a single substitution for water (Figure 57A-C); the resonance of this species fell at 12.7 ppm. This compound was the only species observed, even after heating at 70°C for 15 minutes. Boosting the TCA concentration to 75% and similarly heating for 15 minutes



provided the same results (D); the higher TCA concentration did cause a shift of the resonances by 49 ppm for the tetraaquaplatinum(II) cation, and 66.5 ppm for the mono-substituted TCA complex, as well a broadening of both peaks.

Platinum(IV)

Platinic acid dissolved in 50% TCA showed sequential substitutions of TCA for water over time, analogous to the TFA reactions (Figure 58.) It is important to note, however, that the sequence in which the species grew in was quite different than that observed for the TFA reactions; there appeared to be a kinetic effect acting on the trans- substituted product series which inhibited the rate of formation of these complexes with respect to the cis- products. Note in spectrum B of Figure 58 that the meridional and facial tris- substituted products were in equilibrium before the formation of any trans- bis- species. This appears to be a contradiction: how can triply substituted complexes form and reach equilibrium before those doubly substituted? If the chain of progressive isomeric substitutions in Figure 59 is considered, however, it is clear that if the reaction leg forming the trans- TCA species is kinetically slower, it would be possible to have an equal amount of meridional and facial tris- isomers, without having formed any trans- isomer. Assuming the substitution of ligands on



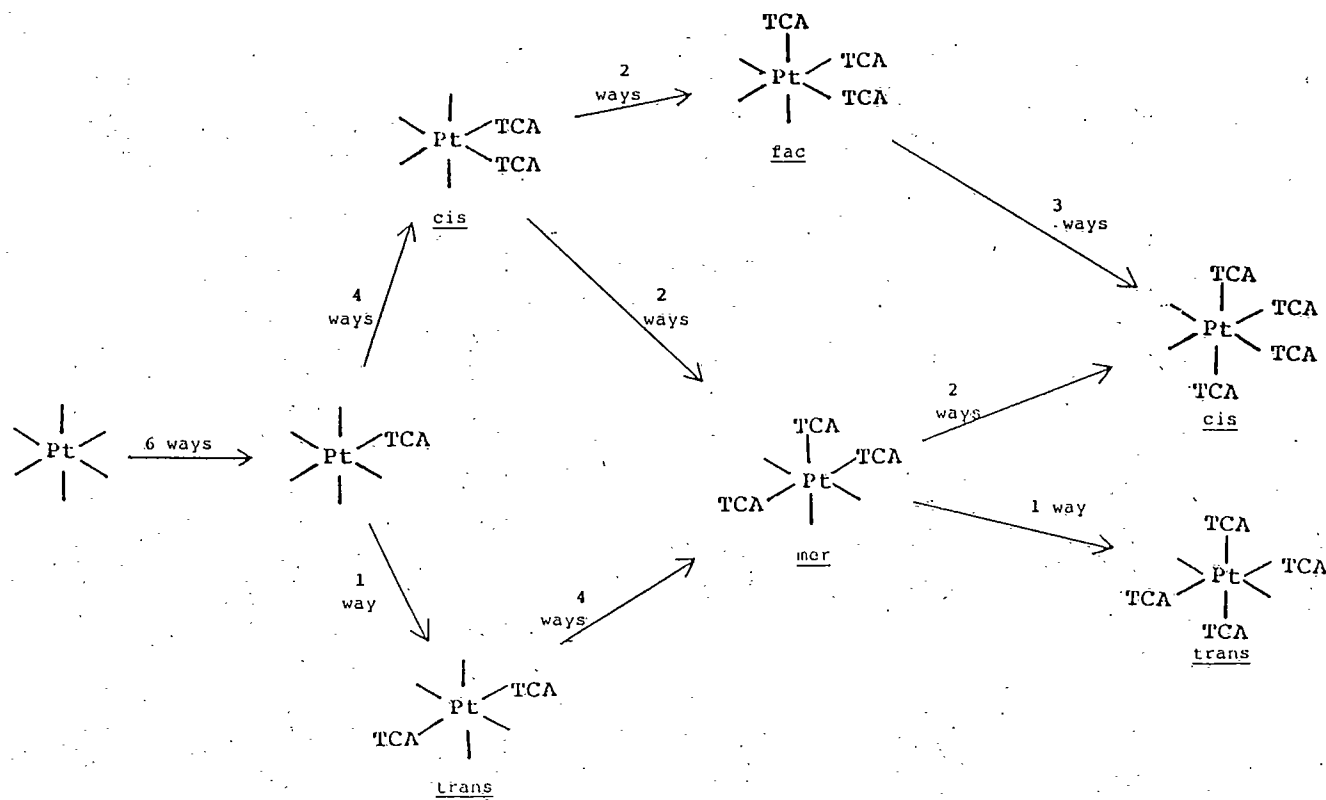


Figure 59. Diagram of Successive TCA Substitutions of Platinic Acid, and their Statistical Likelihood.

the octahedral platinum proceeded through a dissociative mechanism, just based on probability, it is four times as likely that a cis- isomer forms than a trans-; from the cis isomer there is an equal probability that meridional and facial tris- complexes will be formed. It is on this basis that the assignment of the resonances of the two bis- isomers is made; the initially dominant resonance is assigned to the meridional isomer, while the resonance which grows in later must be the facial isomer.

If it is now considered that the chances of forming the cis- substituted tetrakis- species is five times that of forming the trans- isomer, we can assign the resonances of the two tetrakis- complexes as in Figure 58, spectrum E, due to the rapid initial formation of the one isomer over the other. In addition, it can be considered that as the meridional resonance slowly began to grow over time, so too did the new tetrakis peak grow in, indicating an assignment to the trans- species (the facial compound can only give rise to the cis- tetrakis-complex, assigned to the species first observed at 3613.7 ppm, in keeping with the more rapid substitution rate of the cis- derived reactions). It should be noted that the initial fast formation of the cis- derived isomers was eventually countered by the formation of the thermodynamically controlled product distribution; Figure 58 spectra B and D show the transformation of the kinetically

controlled distribution of the tris- isomers (equal concentrations) to the thermodynamically controlled distribution (three times as much meridional isomer as facial).

Methanesulfonic Acid

Platinum(II)

Mixing the tetraaquaplatinum(II) cation with neat methanesulfonic acid (distilled under vacuum) resulted in the formation of four new species; after thirty minutes, the ^{195}Pt NMR spectrum showed no tetraaquaplatinum(II) ion, but new peaks at 281.8, 392.5, 433.3, and 583.7 ppm, assigned to mono-, two bis-, and tris- substituted complexes (Figure 60.) Spectrum A shows the species at 30 minutes, and spectrum C at 17 1/2 hours; note there was little change in the relative intensities of the peaks over this time span, indicating that equilibrium was nearly reached within the first half-hour. The areas of the equilibrated spectra allow the calculation of the equilibrium constants for the formation of three of the species: .06 L/M for each of the two bis-substituted species, and .075 L/M for the tris-substituted complex. The value for the formation of the mono- complex cannot be calculated from this data because we do not know the equilibrium concentration of $\text{Pt}(\text{H}_2\text{O})^{2+}$. The peaks were relatively broad, and shifted several hundred ppm

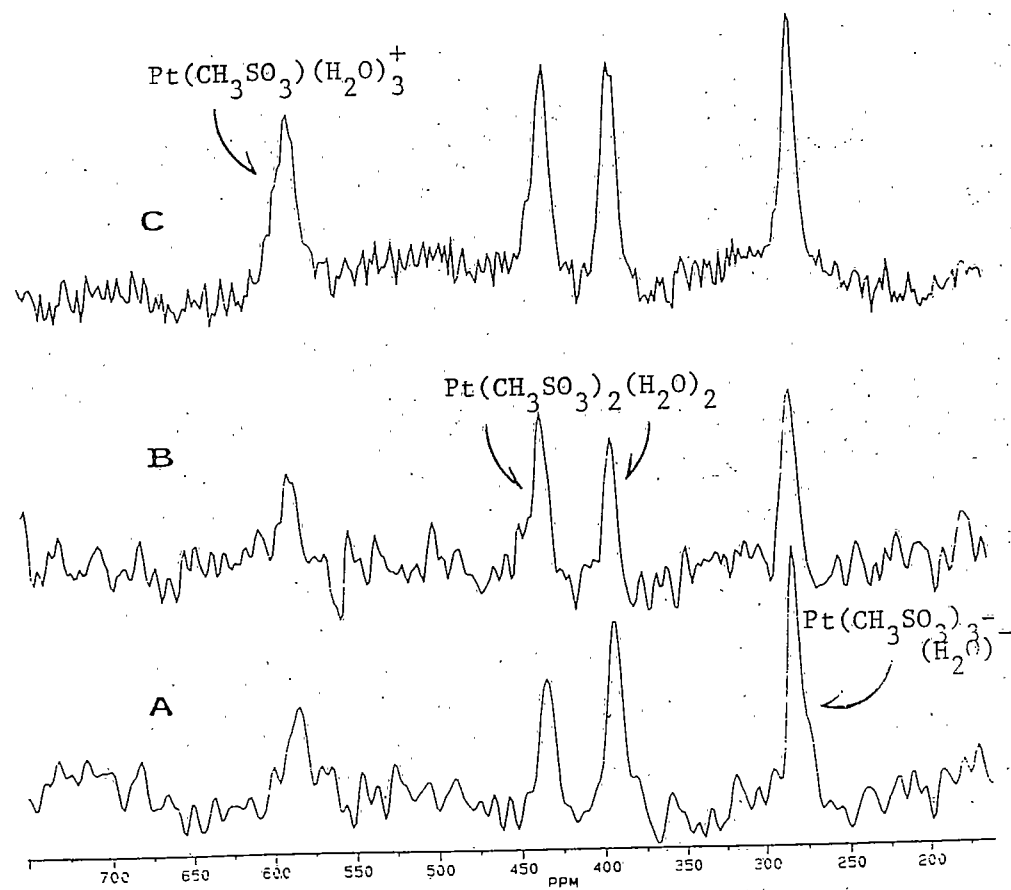


Figure 60. ^{195}Pt NMR Spectrum of Formation of $\text{CH}_3\text{SO}_3\text{H}$ Complexes of $\text{Pt}(\text{H}_2\text{O})_4^{2+}$ in Neat $\text{CH}_3\text{SO}_3\text{H}$.
 (A) 30 Minutes, (B) 9 1/2 Hours, (C) 17 1/2 Hours.

downfield from the chemical shift we would expect for the reaction in 1 M perchloric acid.

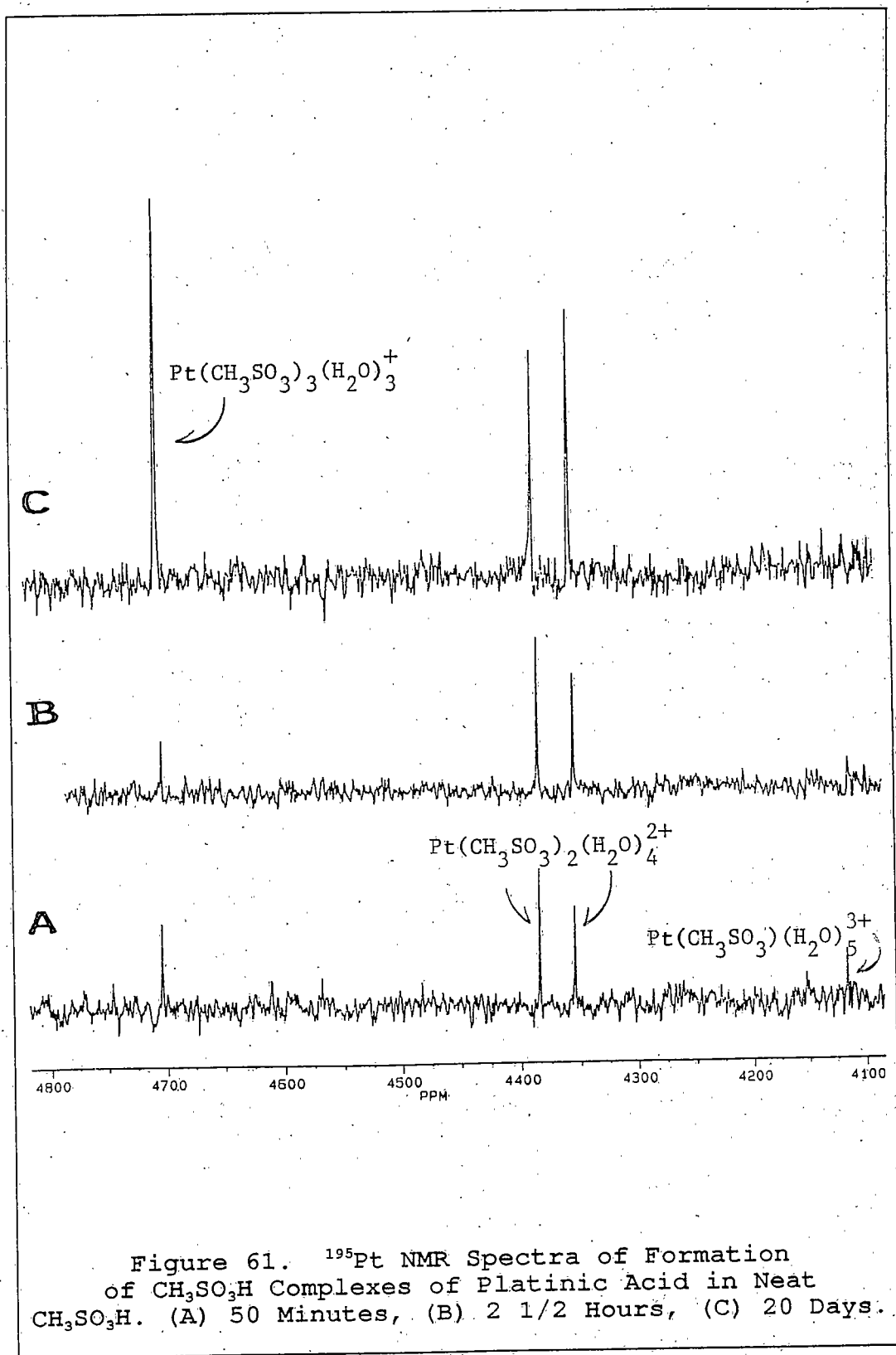
Platinum(IV)

Reaction of platinic acid with vacuum distilled methanesulfonic acid resulted in the initial formation of four species, assigned to progressively more highly substituted methanesulfonic acid complexes the further downfield the chemical shift (Figure 61.) Over time the resonance corresponding to the mono-methanesulfonic acid complex disappeared, with concomitant increases in the concentrations of the remaining three species.

Trifluoromethanesulfonic Acid

Platinum(II) and Platinum(IV)

Reactions of the tetraaquaplatinum(II) cation or platinic acid with dilute and concentrated D₂O solutions of trifluoromethanesulfonic acid (triflic acid), as well as with neat triflic acid, showed no formation of new complexes in the ¹⁹⁵Pt NMR spectrum; only the resonance for Pt(OH)₆²⁻ was observed (and slowly disappeared) for platinum(IV) (Figure 62), and for platinum(II) only the Pt(H₂O)₄²⁺ resonance was seen (Figure 63.) Even with heating at 70°C for 15 minutes, and long data accumulations, no new resonances were observed. This is not unlike the behavior of the strong mineral acids (at least in the case of platinum (IV), and perchloric acid in the



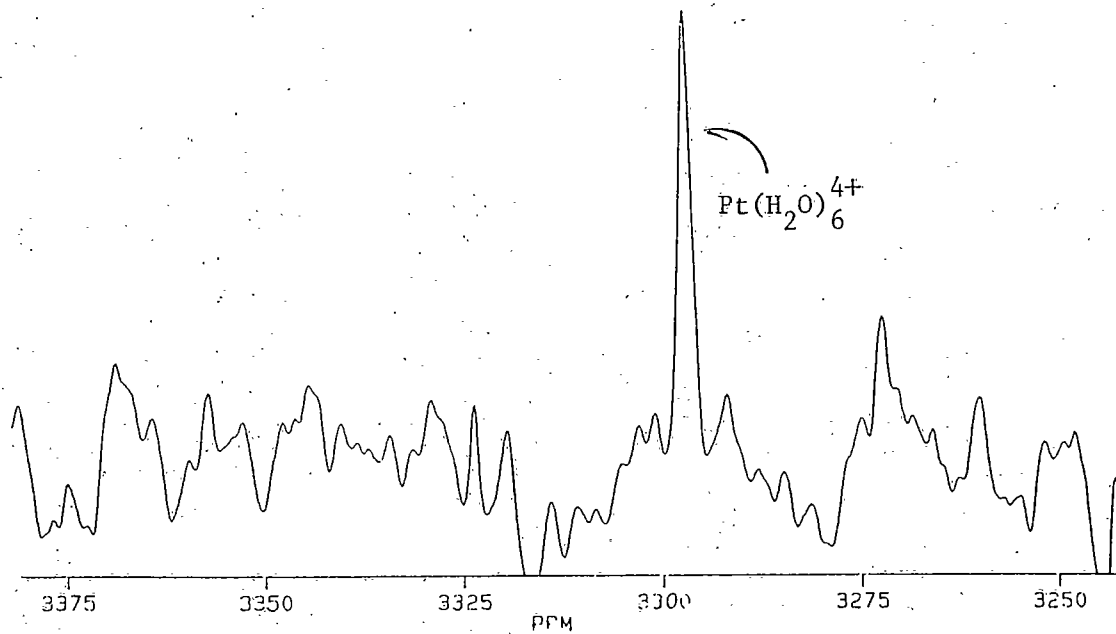


Figure 62. ^{195}Pt NMR Spectrum of Platinic Acid in Triflic Acid.

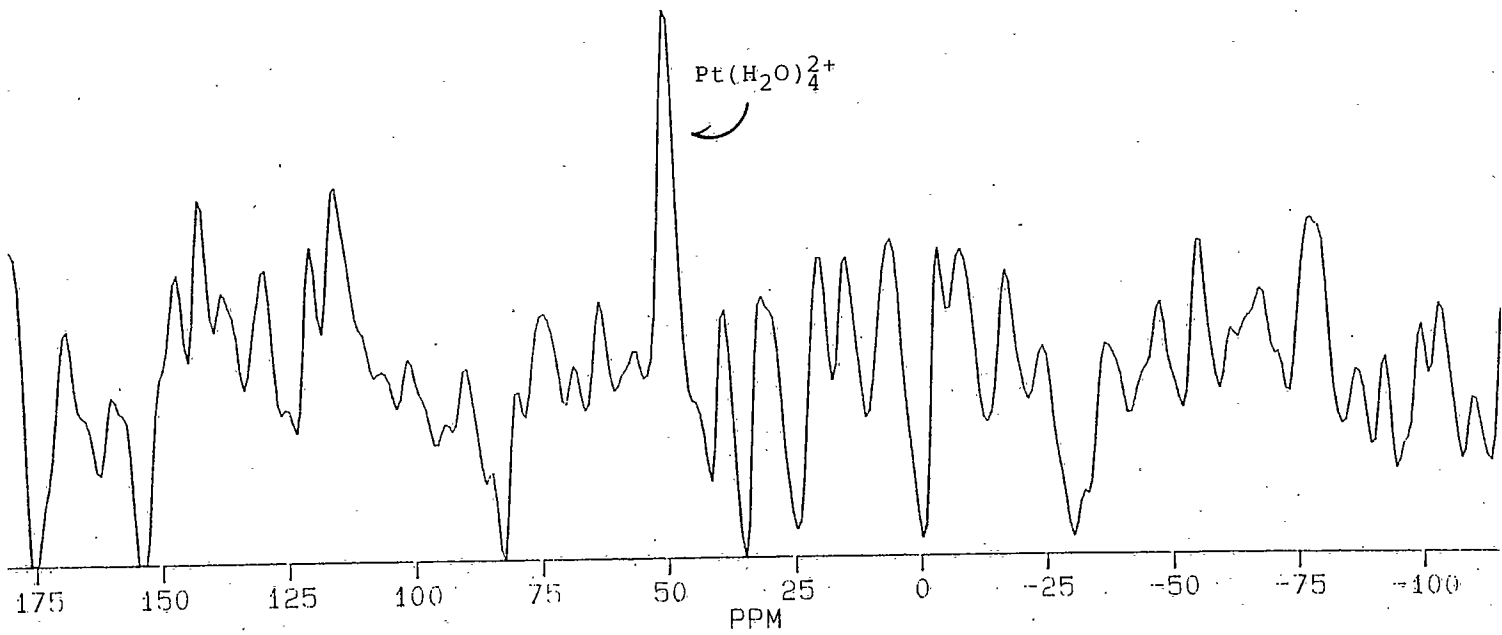


Figure 63. ^{195}Pt NMR Spectra of $\text{Pt}(\text{H}_2\text{O})_4^{2+}$ in Triflic Acid.

case of platinum (II)): for very strong acids, the conjugate base is too weak a ligand to displace coordinated water or hydroxide.

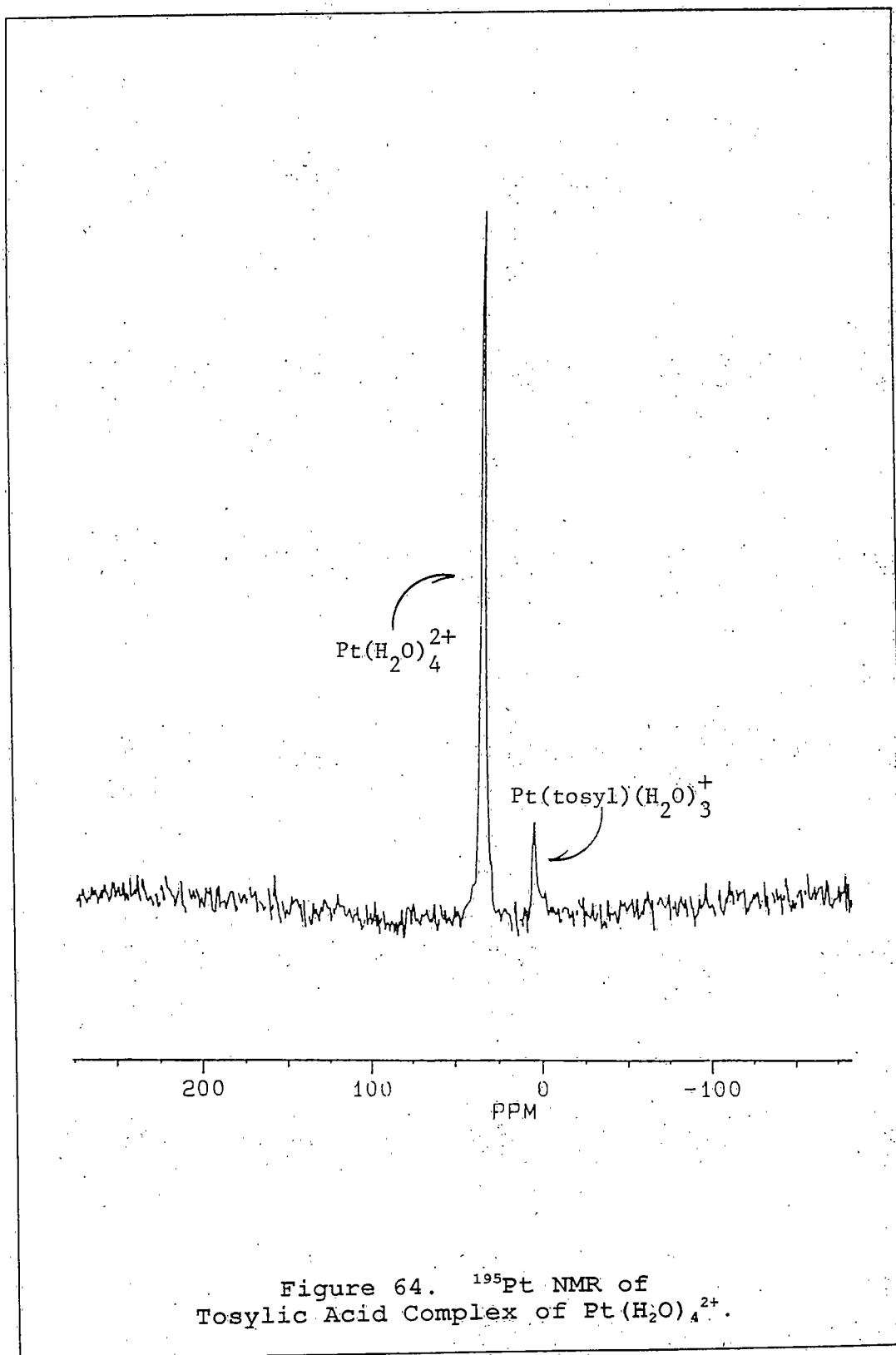
Para-Toluenesulfonic Acid

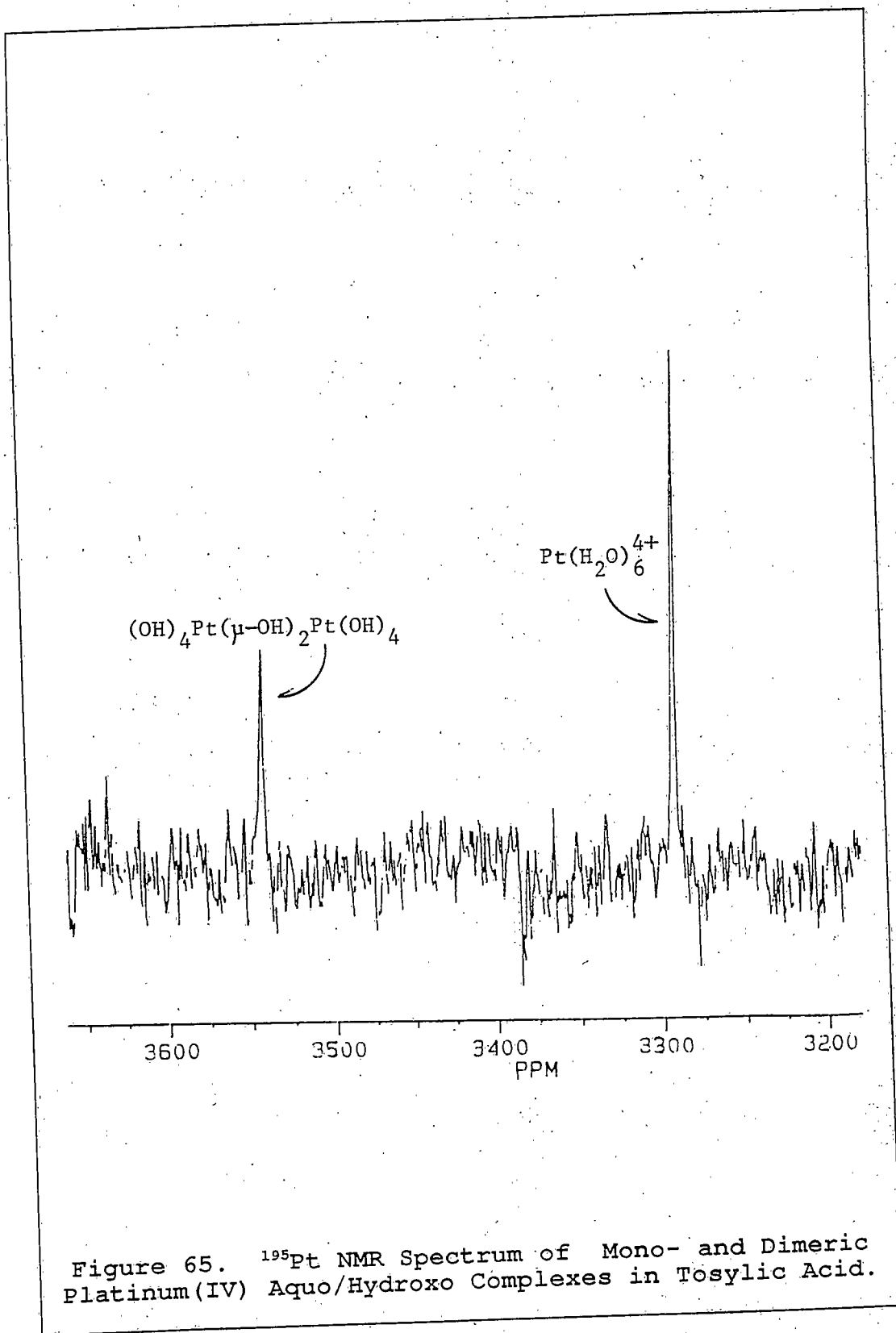
Platinum(II)

The tetraaquaplatinum(II) cation, when dissolved in 50% para-toluenesulfonic acid(tosylic)/D₂O, formed only one species in the Pt NMR spectrum (Figure 64); this species was shifted 33 ppm downfield from the resonance corresponding to tetraaquaplatinum(II), as opposed to the upfield shift commonly observed for such substitutions. As the reaction proceeded over time, the uncoordinated platinum(II) resonance disappeared, with an increase in the remaining singly-coordinated tosylate complex resonance.

Platinum(IV)

Solutions of platonic acid in 50% tosylic acid/D₂O showed no new resonances in the ¹⁹⁵Pt NMR spectrum (Figure 65.) Even after 24 hours and heating at 70°C for 15 minutes, the only peaks observed are those for the neutral platonic acid and the platinum(IV) hydroxo-bridged dimer.





CHAPTER IV

CONCLUSIONS

A number of concepts and results have been presented in this work; a brief synopsis of the important facts we have learned and principles we have demonstrated follows.

Compounds of high nuclearity can be prepared by thermal and vacuum dehydration of platinum complexes formed with phosphorous acid; this oligomerization might be controlled to sequentially form desired polynuclear complexes.

The synthesis and physical properties of an intensely red luminescent platinum cluster of high nuclearity has been reported; the solution stability and reactivity of three separate salts has been studied, and as a result of physical measurements (especially elemental analysis) we have enough information to propose a structure containing a polymeric pentanuclear pyrophosphite bridged anion: $(\text{CH}_3(\text{C}_6\text{H}_5)_3\text{P})_6[\text{Pt}_5(\text{P}_2\text{O}_5\text{H}_2)_8(\text{P}(\text{OH})_3)_4] \cdot 4\text{H}_2\text{O}$.

The reported facile polymerization of platinum(IV) in strongly acidic mineral acids has been confirmed; this polymerization occurred without change in oxidation state, and occurred as readily in nonaqueous as in aqueous media. The platinum(IV) dimer $(\text{OH})_4\text{Pt}(\mu\text{-OH})_2(\text{OH}-$

$\text{Pt}(\text{OH})_4^{2-}$ is much more stable to olation in acid than is the mononuclear complex $\text{Pt}(\text{OH})_6^{2-}$.

The pronounced oligomerization of platinum(IV) under conditions without oxygen ligands available for bridge formation (non-aqueous media) suggests a mechanism of polymerization that must involve intermolecular dehydration of coordinated hydroxide and water to permit the olation of the polynuclear molecules.

The platinum NMR resonances of platinum(II) and platinum(IV) complexes shift steadily downfield as solution acidity increases.

Platinum(IV), under less acidic conditions with strong organic acids (which must act as better bases than the conjugate bases of strong mineral acids), forms highly substituted complexes showing geometric isomerism. Eighteen new complexes of this kind have been identified by platinum NMR spectroscopy and the geometrical isomers assigned.

Under some conditions platinum(II) appears to polymerize in acid solution; this was observed when platinum(III) complexes decomposed over time, or when platinum(IV) and platinum(II) species were mixed in solution.

Using ^{195}Pt NMR spectroscopy, fourteen new platinum(II) complexes have been reported and identified: eleven complexes with strong organic acids, two complexes

with nitrate/TFA coordination, and one in concentrated sulfuric acid.

The formation constants for seven different species formed by the reaction of platinum(II) with TFA and methanesulfonic acid have been calculated from NMR spectra; they are 3.0 L/M for $\text{Pt}(\text{H}_2\text{O})_3(\text{TFA})_1^+$, 1.05 L/M for the two $\text{Pt}(\text{H}_2\text{O})_2(\text{TFA})_2$ species, and 0.42 L/M for $\text{Pt}(\text{H}_2\text{O})(\text{TFA})_3^-$; 0.06 L/M for the two $\text{Pt}(\text{H}_2\text{O})_2(\text{CH}_3\text{SO}_3)_2$ species, and 0.075 L/M for $\text{Pt}(\text{H}_2\text{O})(\text{CH}_3\text{SO}_3)_3^-$.

TFA and TCA react with platinum(II) in air to form blue solutions like those proposed to be extended chain interactions (104) like acetic acid does.

Platinum(III) dimers decompose to form platinum(II) and platinum(IV) compounds in the presence of strongly coordinating ligands like chloride; no platinum(III) mononuclear complexes were observed.

Evidence for the formation of platinum(II)-platinum(IV) mixed metal complexes in strong acid has been reported.

It has been shown the formation of platinum(III) dimers can proceed through a mechanism of reverse disproportionation.

The reverse disproportionation method has been used to synthesize a new platinum(III) TFA dimer identified based upon its ^{195}Pt NMR chemical shift.

REFERENCES CITED

1. Browning, P.E. "Introduction to the Rarer Elements", 2nd. ed. Jone Wiley and Sons, New York, 1908, p.161.
2. de Ulloa, D.A. *Phil. Trans. Roy. Soc.*, 1750, **XLVI**, 584.
3. Greenwood, N.N.; Earnshaw, A. "Chemistry of the Elements" Pergamon Press, Oxford, 1984, p.1328.
4. Blondel, M. *Ann. Chim. Phys.*, 1905, **8**, 110.
5. Tschugaev, L.; Skanavy-Grigomeva, M.; Posniak, A. *Zh. Anorg. Chem.*, 1925, **148**, 37.
6. Calabrese, J.C., et. al. *J. Am. Chem. Soc.*, 1974, **96**, 2616.
7. Feltham, R.D., et.al. *Inorg. Chem.*, 1985, **24**, 1503.
8. Struchkov, Y.T., et.al. *J. Organomet. Chem.*, 1986, **301**, C35.
9. Mingos, D.M.P., et.al. *J. Chem. Soc. Dalton Trans.*, 1986, 1535.
10. Teo, B.K., et.al. *Inorg. Chem.*, 1986, **25**, 2262.
11. Hartley, F.R. Vol. 6, Chapter 39, "Comprehensive Organometallic Chemistry" Pergamon Press, Oxford, 1982.
12. Carrondo, M.A.A.F. de C.T., et.al. *J. Chem. Soc. Chem. Comm.*, 1976, 410.
13. Kuype, J.; Vrieze, K. *Trans. Met. Chem.*, 1976, **1**, 208.
14. Overbeck, A. R., et.al. *Inorg. Chem.*, 1978, **17**, 1938.
15. Bell, H.C., et.al. *Inorg. Chem.*, 1983, **22**, 444.
16. Cotton, F.A., et.al. *Rev. Chim. Minerale.*, 1983, **20**, 496.
17. Peterson, E.S., p.H.D. Thesis, Montana State University, October, 1987.

18. Hofmann, K.A.; Bugge, G. *Ber.*, 1907, **40**, 1777.
19. Hofmann, K.A.; Bugge, G. *Ber.*, 1908, **41**, 312.
20. Rosenberg, B.; Van Camp, L.; Trasko, J.E., Mansour, U.H. *Nature*, 1969, **222**, 385.
21. Arrizabalaga, P., et.al. *Inorg. Chem.*, 1985, **24**, 3656, and references therein.
22. Davidson, P.J., et.al. *Cancer Chemotherp. Rep.*, 1975, **59**, 287.
23. Rosenberg, B., et.al. *Cancer Chemotherp. Rep.*, 1975, **59**, 589.
24. Speer, R.J., et.al. *Cancer Chemotherp. Rep.*, 1975, **59**, 629.
25. Barton, J.K., et.al. *J. Am. Chem. Soc.*, 1979, **101**, 1434.
26. Matsumoto, K.; Watanabe, T. *J. Am. Chem. Soc.*, 1986, **108**, 1308.
27. Vezes, M. *Ann. Chem. Phys.*, 1893, **22**, 160.
28. Vezes, M. *Z. Anorg. Chem.*, 1897, **14**, 278.
29. Underhill, A.E.; Watkins, D.M. *J. Chem. Soc. Dalton Trans.*, 1977, 5.
30. Ginzberg, S.I., et.al. *Zh. Neorg. Khim.*, 1969, **14**(12), 3337.
31. Sofronkova, G.M., et.al. *Izv. Sib. Otd. Akad. Nauk. SSSR, Ser. Khim. Nauk.*, 1970, **4**, 105.
32. Ivonova, S.N., et.al. *Izv. Sib. Otd. Akad. Nauk. SSSR, Ser. Khim. Nauk.*, 1971, **6**, 38.
33. Muraveiskaya, G.S., et.al. *Tezisy. Dokl. - Vses. Chugaevsko-Soveschch. Khim. Kompledsn. Soedin.*, 12th, 1975, **3**, 372.
34. Orlova, V.S., et.al. *Zh. Neorg. Khim.*, 1975, **20**(5), 1340.

35. Nuraveiskaya, G.S., et.al. *Dokl. Akad. Nauk. SSSR*, 1976, 226(3), 596.
36. Cotton, F.A., et.al. *Inorg. Chem.*, 1974, 14, 391.
37. Cotton, F.A., et.al. *Inorg. Chem.*, 1975, 14, 391.
38. Bancroft, D.P., et.al. *Inorg. Chem. Acta.*, 1984, 87, 147.
39. Falohon, et.al. *Inorg. Chem.*, 1982, 21(7), 2889.
40. Cotton, F.A., et.al. *Inorg. Chem.*, 1974, 14, 649.
41. Cotton, F.A., et.al. *Inorg. Chem.*, 1975, 14, 391.
42. Dikareva, L.M.; Zefirov, Yu.V.; Zhilyaev, A.N.; Baranovskii, I.B.; Porai-Kashits, M.A. *Zh. Neorg. Khim.*, 32(1), 115.
43. Bakhvalova, I.P.; Voldova, G.V.; Ivanov, V.M. *Zh. Anal. Khim.*, 1990, 45(3), 496.
44. Ginzburg, S.I.; Yuz'ko, M.I.; Sal'skaya, L.G. *Zhur. Neorg. Khim.*, 1963, 8, 839.
45. Ginzburg, S.I.; Yuz'ko, M.I.; Fomina, T.A. *Zhur. Neorg. Khim.*, 1966, 11, 2551.
46. Koz'min, P.A.; Larina, T.B.; Surazhskaya, M.D.; Kotel'nikova, A.S.; Osmanov, N.S. *Koord. Khim.*, 1980, 6(8), 1264.
47. Peterson, E.S.; Larsen, R.D.; Abbott, E.H. *Inorg. Chem.*, 1988, 27, 3514.
48. Min, D.; Larsen, R.D.; Abbott, E.H. *Inorg. Chem.*, 1990, 29, 73.
49. Appleton, T.G.; Hall, J.R.; Neale, D.W.; Ralph, S.F. *Inorg. Chim. Acta.*, 1983, 77, L149.
50. Appleton, T.G.; Hall, J.R.; Neale, D.W. *Inorg. Chim. Acta.*, 1985, 104, 19.
51. Muraveiskaya, G.S., et.al. *Koord. Khim.*, 1908, 6, 463.

52. Conder, H.L. *Inorg. Chem.*, 1983, 22, 1887.
53. Dikareva, L.M.; Sadikov, G.G.; Porai-Koshits, M.A.; Baranovskii, I.B.; Abdullaev, S.S.; Shchelodov, R.V. *Zh. Neorg. Khim.*, 1982, 27(2), 417.
54. Korsunskii, V.I. *Zh. Strukt. Khim.*, 1987, 28(1), 80.
55. Grinberg, A.A. *Dokl. Akad. Nauk SSSR*, 1955, 155, 1256.
56. Troitskaya, A.D. *Russ. J. Inorg. Chem.*, 1961, 6, 585.
57. Sperline, R.P.; Dickson, M.K.; Roundhill, D.M. *J. Chem. Soc. Chem. Comm.*, 1977, 62.
58. Che, C.-M.; Butler, L.G.; Grunthaner, P.J.; Gray, H.B. *Inorg. Chem.*, 1985, 24, 4662.
59. Filomena Dos Remedios Pintos, M.A.; Sadler, P.J.; Neidle, S.; Sanderson, M.R.; Subbiah, A.; Kuroda, R. *J. Chem. Soc. Chem. Comm.*, 1908, 13.
60. Dickson, M.K.; Fordyce, W.A.; Appel, D.M.; Alexander, K.; Stein, P.; Roundhill, D.M. *Inorg. Chem.*, 1982, 21, 3857.
61. Sigal, I.S.; Gray, H.B.; *J. Am. Chem. Soc.*, 1981, 103, 2220.
62. Mann, K.R.; Gordon, J.G., II; Gray, H.B. *J. Am. Chem. Soc.*, 1975, 97, 3553.
63. Mann, K.R.; Lewis, N.S.; Williams, R.M.; Gray, H.B.; Gordon, J.G., II *Inorg. Chem.*, 1978, 17, 828.
64. Hollis, L.S.; Roberts, M.M.; Lippard, S.J. *Inorg. Chem.*, 1983, 22, 3637.
65. Che, W.P.; Schaefer, W.P.; Gray, H.B.; Dickson, M.K.; Stein, P.B.; Roundhill, D.M. *J. Am. Chem. Soc.*, 1982, 104, 4253.
66. Alexander, K.A.; Bryan, S.A.; Fronczek, F.R.; Fultz, W.C.; Rheingold, A.L.; Roundhill, D.M.; Stein, P.; Watkins, S.F. *Inorg. Chem.*, 1985, 24, 2803.

67. Clark, R.J.H.; Kurmoo, M.; Dawes, H.M.; Hursthouse, M.B. *Inorg. Chem.*, 1986, **25**, 409.
68. Hedden, D.; Roundhill, D.M.; Walkinshaw, M.D. *Inorg. Chem.*, 1985, **24**, 3146.
69. Che, C.-M.; Mak, T.C.W.; Gray, H.B. *Inorg. Chem.*, 1984, **23**, 4386.
70. Bryan, S.A.; Dickson, M.K.; Roundhill, D.M. *J. Am. Chem. Soc.*, 1984, **106**, 1882.
71. Che, C.-M.; Herbststein, F.J.; Schaefer, W.P.; Marsh, R.F.; Gray, H.B. *J. Am. Chem. Soc.*, 1983, **105**, 4604.
72. Kurmoo, M.; Clark, R.H.J. *Inorg. Chem.*, 1985, **24**, 4420.
73. Gustafson, R.L.; Martell, A.E. *J. Am. Chem. Soc.*, 1959, **81**, 525.
74. Stuntzi, H.; Marty, W. *Inorg. Chem.*, 1983, **22**, 2145.
75. Anderson, P.; Damhus, T.; Pedersen, F.; Petersen, A. *Acta. Chem. Scand.*, 1984, **A38**, 359.
76. Stuntzi, H.; Rotzinger, F.P.; Marty, W. *Inorg. Chem.*, 1984, **23**, 2160.
77. Kauffman, G.B.; Pinnell, R.P. *Inor. Synth.*, 1960, **6**, 176.
78. Searle, G.H.; Hambley, T.W. *Aust. J. Chem.*, 1982, **35**, 1297.
79. Wieghardt, K.; Chaudhuri, P.; Nuber, B.; Wiess, J. *Inorg. Chem.*, 1982, **21**, 3086.
80. Tanaka, I., et al. *Bull. Chem. Soc. Jpn.*, 1983, **56**, 657.
81. Oro, L.A., et al. *J. Chem. Soc. Dalton Trans.*, 1984, 1823.
82. Castillo-Blum, S.E.; Richens, D.T.; Sykes, A.G. *J. Chem. Soc. Chem. Comm.*, 1986, 1120.

83. Wells, A.F. "Structural Inorganic Chemistry", 4th ed., Ch. 13, Oxford, University Press, Oxford, 1975, pp. 476-515.
84. Simon, A., et al. *Angew. Chem. Int. Ed. Engl.*, 1987, **26**, 139.
85. Mont, G.E.; Martell, A.E. *J. Am. Chem. Soc.*, 1966, **88**, 1387.
86. Faggiani, R.; Lippert, B.; Lock, C.J.L.; Rosenberg, B. *Inorg. Chem.*, 1977, **16**(5), 1192.
87. Faggiani, R.; Lippert, B.; Lock, S.J.L.; Rosenberg, B. *J. Am. Chem. Soc.*, 1977, **99**, 777.
88. Rochon, F.P.; Morneau, A.; Melanson, R. *Inorg. Chem.*, 1988, **27**, 10.
89. Rochon, F.P.; Kong, P.-Ch.; Girard, L. *Can. J. Chem.*, 1986, **64**, 1897.
90. Rochon, F.P.; Girard, L. *Can. J. Chem.*, 1986, **64**, 1974.
91. Bushnell, G.W., et al. *Can. J. Chem.*, 1972, **50**, 3694.
92. Sidgwick, N.V. "Chemical Elements and Their Compounds", Clarendon Press, Oxford, 1962, p. 1610.
93. Nabivanets, B.I.; Kalabina, L.V.; Kudritskaya, L.N. *Russ. J. Inorg. Chem.*, 1971, **16**(12), 1736.
94. Volynets, M.P.; Ermakov, A.N.; Ginzberg, S.I.; Fomina, T.V.; Fomina, T.A. *Zh. Analyt. Khim.*, 1972, **27**(7), 1322.
95. Ginzburg, S.I.; Dubrovskaya, G.M.; Yuz'ko, M.I.; Evstaf'va, O.N.; Kharitonov, Yu.Ya. *Russ. J. Inorg. Chem.*, 1975, **20**(5), 758.
96. Nabivanets, B.I.; Kalabina, L.V.; Kutsyi, V.G. *Russ. J. Inorg. Chem.*, 1988, **33**(11), 1658.
97. Weissberger, A. *American Scientist*, 1970, **58**, 648.

98. Beaulieu, W.B.; Rauchfuss, R.B.; Roundhill, D.M. *Inorg. Chem.*, 1975, 14, 1732.
99. Kong, P-C.; Roundhill, D.M. *J. Chem. Soc. Dalton Trans.*, 1974, 187.
100. Dixon, K.R.; Rattray, A.D. *Canad. J. Chem.*, 1971, 49, 3997.
101. Corbridge, D.E.C. "Topics in Phosphorus Chemistry", vol. 6, p.234, Grayson, M. and Griffith, E.J., eds., Interscience Publishers, New York, 1969.
102. Stein, P.; Dickson, M.K.; Roundhill, D.M. *J. Am. Chem. Soc.*, 1983, 105, 3489.
103. Che, C.-M.; Butler, L.G.; Gray, H.B. *J. Am. Chem. Soc.*, 1981, 103, 7796.
104. Carr, C.; Goggin, P.L.; Goodfellow, R.J. *Inorg. Chim. Acta.*, 1984, 81, L25.
105. Elding, L.I. *Acta Chem. Scand.*, 1970, 24, 1331.
106. Appleton, T.G.; Hall, J.R.; Ralph, S.F.; Thompson, C.S.McK. *Inorg. Chem.*, 1984, 23, 3521.
107. Bellucci, I. *Z. Anorg. Allg. Chem.* 1905, 44, 168.
108. Bandel, V.G.; Platte, C.; Tromel, M. *Z. Anor. Allg. Chem.*, 1981, 472, 95.
109. Groning, O.; Elding, L.I. *Inorg. Chem.*, 1989, 28, 3366.
110. Wilmarth, W.K.; Haim, A. "Peroxide Oxidation Mechanisms", Edwards, J.O., ed., p. 175, Interscience Publishers, New York, 1962.

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